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LI. *Some Remarks on the Analogy of certain Cases of Propagation of Electromagnetic Waves and the Motion of a Particle in a Potential Field.* By W. DE GROOT, *D.Sc.**

§ 1. *Summary.*

In §§ 2–6 the conditions are investigated for which a wave-equation of the type

$$\Delta\phi + \frac{\omega^2}{u^2}\phi = 0$$

may be such that a group of waves moves as a mass-point in a field of force which is independent of the frequency of the group. This leads to either the relativistic or the non-relativistic Schrödinger-equation for the dependence of u on ω.

In the case of the propagation of electromagnetic waves in a medium containing charged particles, the movement of a group of waves may also be made to correspond to that of a particle in a potential field of force; in this case the potential, however, depends on ω (§§ 7, 8).

In §§ 9–12 the formulæ derived in the foregoing paragraphs are applied to the case of radio-waves reflected by the Heaviside-Kennelly layer, and it is shown that the problem of finding the height of the layer, *i. e.* the determination of the concentration n of the electrons as a function of the height z from group-time measurements, is related to the

* Communicated by Prof. E. V. Appleton, F.R.S.

integral-equation of the "tautochrone" as solved by Abel (1829).

In § 13 it is shown that if z is a multivalued function of n the problem becomes indefinite.

In § 14 the bending of the rays round the earth and the calculation of the "effective height" is treated.

In § 15 possible objections to the calculations contained in this article are anticipated.

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§ 2. IN the next paragraphs we investigate the conditions which allow us to replace a problem of wave-propagation by that of the motion of a particle in a potential-field *.

It is known that under certain restrictions the differential equation which governs the propagation of a disturbance in a non-homogeneous medium can be solved by an expression of the form

$$\phi(x, y, z)e^{j\omega t} = \mathrm{A}(x, y, z)e^{j\{\omega t - \mathrm{S}(x, y, z)\}} \quad . \quad . \quad (1)$$

Equation (1) represents a monochromatic wave of frequency ω and amplitude A, whilst the surfaces

$$\mathrm{S} = \text{const.}$$

are surfaces of equal phase. We will, however, limit our considerations to the cases in which the differential equation just mentioned, after substitution of the left-hand part of equation (1), changes into an "amplitude equation" of the form

$$\Delta\phi + \frac{\omega^2}{u^2}\phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where u, the phase velocity, may depend on x, y, z †.

The restrictions alluded to may then be put in the form: The variations of the quantities A and S, as a function of x,

* I am indebted to Dr. B. van der Pol, Eindhoven, and to Prof. E. V. Appleton, London, who, in discussions on the propagation of radio-waves in the upper atmosphere, stimulated the investigations contained in this article. Prof. Appleton proposed the problem of the determination of the true height reached by wireless waves in a recent lecture at Eindhoven. The idea that the Schrödinger wave-equation might be of any use in this respect was suggested to us by Prof. G. Manneback (Leuven).

† A review of the questions referred to in this section, from a much broader point of view, is to be found in a series of lectures by A. D. Fokker (Dutch) entitled: "Inleiding tot de golvings- en quantum-mechanica" (*i. e.*, "Introduction to the Wave- and Quantum-mechanics"), Haarlem (Holland), De Erven Loosjes, 1928 (Chap. I.), and, further, in A. Sommerfield "Atombau," Ergänzungsband, Braunschweig, Vieweg-Sohn (Chap. III., Section 1).

y, z, must be "slow." This leads to the following two conditions:

(a) The radius of curvature of the surfaces S = const. must be large with respect to the local wave-length

$$R >> \lambda.$$

(b) The relative variation of the quantity u, when proceeding in the direction of its gradient along a distance equal to the local wave-length, must be small—

$$\frac{\lambda}{u} \left| \text{grad } u \right| << 1.$$

§ 3. Supposing the conditions (a) and (b) to be fulfilled, it is generally possible to consider a portion of space where the surfaces

$$u(\omega, x, y, z) = \text{const.} \quad (\omega = \text{const.})$$

are to be considered as parallel planes.

In this portion of space Snell's law is valid, so that

$$\frac{u}{\sin \theta} = \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where θ is the angle between the normal of the surfaces of equal phase (ray) and the gradient of u. If, now, we wish to construct a potential distribution

$$V(x, y, z),$$

so that the motion of a particle imitates the motion of the waves, it is clear that the surfaces u = const. must also be the surfaces V = const. If this were not the case, a particle starting along the gradient of u would not follow the corresponding ray. Since θ is also the angle between the direction of motion of the particle and the potential gradient,

$$v \sin \theta = \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where v is the velocity of the particle. It follows, therefore, from (4) and (5) that

$$u \, . \, v = \text{const. (K say)}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

§ 4. The actual properties of V depend on the kind of mechanics we wish to adopt for the particle. We consider first non-relativistic classical mechanics, for which

$$E = V + \tfrac{1}{2} M v^2 = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It follows from (5) and (6)

$$V = E - \tfrac{1}{2} M v^2 = E - \frac{M K^2}{2u^2} \quad . \quad . \quad . \quad . \quad (7)$$

We consider first the specifications necessary to make the function V independent of the frequency (condition I.).

It will be understood that this limits the form of the function u, because a surface $u=$const. must remain the same in changing over from one frequency to another. At the same time we attempt to fulfil a condition of quite another type, namely, that the velocity of a "group" of waves shall coincide with the velocity of the particle (condition II.). In order to fulfil the conditions I. and II. we make E and K depend on ω.

Then condition II. leads to

$$\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)=\frac{1}{v}=\sqrt{\frac{\mathrm{M}}{2\{\mathrm{E}(\omega)-\mathrm{V}(x,\,y,\,z)\}}}, \quad . \quad . \quad (8)$$

whilst

$$u.v=u:\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)=\mathrm{K}(\omega). \quad . \quad . \quad . \quad . \quad (9)$$

From (9) it is seen immediately that it will be in general impossible to fulfil the conditions I. and II.

§ 5. From (8) and (9) the special kind of dispersion-law, for which it is possible to fulfil (I.) and (II.) (§ 4), may be derived; according to (9)

$$\frac{1}{u}\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)=\frac{1}{\mathrm{K}(\omega)}.$$

Thus

$$\left(\frac{\omega}{u}\right)^2=\int\frac{2\omega}{\mathrm{K}(\omega)}\,d\omega=\mathrm{H}(\omega)+\mathrm{F}(x,\,y,\,z), \quad . \quad . \quad (10)$$

so that

$$\frac{\omega}{u}=\sqrt{\mathrm{H}(\omega)+\mathrm{F}(x,\,y,\,z)} \quad . \quad . \quad . \quad . \quad (11)$$

and

$$\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)=\frac{\frac{1}{2}\partial\mathrm{H}/\partial\omega}{\sqrt{\mathrm{H}(\omega)+\mathrm{F}(x,\,y,\,z)}} \quad . \quad . \quad . \quad (12)$$

Comparing this last expression with (8), it is seen that we are compelled to take

$$\frac{\partial\mathrm{H}}{\partial\omega}=\text{const.}$$

and

$$\mathrm{H}=a\omega+b\,;$$

and, as E must be proportional to H,

$$\mathrm{E}=h\omega-k.$$

Putting $H=\gamma E$ and $F=-\gamma V$ one easily finds that γ must be equal to $2M/h^2$, which reduces (11) to

$$\frac{\omega}{u}=\frac{1}{h}\sqrt{2M(h\omega-k-V)}=\frac{1}{h}\sqrt{2M(E-V)} \quad . \quad (13)$$

$$u=\frac{h\omega}{\sqrt{2M(h\omega-k-V)}}=\frac{E+k}{\sqrt{2M(E-V)}}. \quad . \quad (14)$$

From (13) it follows that the amplitude equation (2) reduces to the form

$$\Delta\phi+\frac{2M}{h^2}(E-V)\phi=0. \quad . \quad . \quad . \quad . \quad (15)$$

We see, therefore, that conditions I. and II. lead to the special form of amplitude-equation introduced into physics by Schrödinger *.

In the case of Schrödinger's equation a special value is attributed to the constant h, namely, $\frac{1}{2}\pi$ times the Planck constant $=(6{\cdot}55:2\pi).10^{-27}$. It will be clear that this value is of no interest for us now.

§ 6 We will derive now the equation corresponding to the conditions I. and II. in the case of the particle being subjected to relativistic mechanics. It is sufficient to replace in the equation

$$\frac{d}{dt}Mv_x=-\frac{\partial V}{\partial x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

the constant M by $M/\sqrt{(1-v^2/c^2)}$, where M is again a constant and represents the mass of the particle at rest. It follows, when x is the projection of the ray on the planes of equal potential, that instead of equation (4) we get

$$\frac{v\sin\theta}{\sqrt{1-v^2/c^2}}=\text{const.}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

so that instead of (5) we get

$$u.v=\text{const.}\sqrt{1-v^2/c^2}, \quad . \quad . \quad . \quad . \quad (18)$$

where the constant may be a function of ω. On the other hand, we have to consider the total energy $E+Mc^2$ (where

* E. Schrödinger: Four Lectures on Wave Mechanics (London, Blackie & Son, 1928). In the first of these lectures the equation (14) is derived with the constant k equal to zero. As will be seen further on, it proves better not to cancel the constant k, because when one tries to derive equation (14) from the corresponding relativistic equation supposing the particle velocity small, one finds $k=Mc^2$.

E is the sum of kinetic and potential energies) as being a function of ω ($f(\omega)$, say), so that the kinetic energy proves to be

$$\frac{Mc^2}{\sqrt{1-v^2/c^2}} - Mc^2 = E - V = f(\omega) - Mc^2 - V, \quad . \quad (19)$$

from which follows

$$\frac{v}{c} = \frac{\sqrt{(f-V)^2 - M^2c^4}}{f-V} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Combining with (18) and (19), we get:

$$u = \frac{g(\omega)}{\sqrt{(f-v)^2 - M^2c^4}}, \quad . \quad . \quad . \quad . \quad (21)$$

$$\frac{\omega}{u} = j(\omega)\sqrt{(f-v)^2 - M^2c^4}, \quad . \quad . \quad . \quad (22)$$

where $j(\omega) = \omega : g(\omega)$, and

$$\frac{d}{d\omega}\left(\frac{\omega}{u}\right) = \frac{j \cdot f'(f-v)}{\sqrt{(f-v)^2 - M^2c^4}} + j'\sqrt{(f-v)^2 - M^2c^4} \quad (23)$$

(where the dot denotes derivation with respect to ω). Comparing this with (20), it follows that j' must be zero, so that j is a constant (p say) and $f' = 1/cp = h$. It follows that

$$Mc^2 + E = h\omega - k,$$

where k is arbitrary. If k is put equal to zero,

$$E + Mc^2 = h\omega, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

so that from (21) we find for u:

$$u = \frac{ch}{\sqrt{(h\omega - V)^2 - M^2c^4}}, \quad . \quad . \quad . \quad . \quad (25)$$

$$\frac{\omega}{u} = \frac{1}{h}\sqrt{\frac{(h\omega - V)^2}{c^2} - M^2c^2}; \quad . \quad . \quad (26)$$

from (26) it follows that the amplitude equation is now

$$\Delta\phi + \frac{1}{h^2}\left\{\frac{(h\omega - V)^2}{c^2} - M^2c^2\right\}\phi = 0, \quad . \quad . \quad (27)$$

or

$$\Delta\phi + \frac{1}{h^2}\left\{\frac{(E + Mc^2 - V)^2}{c^2} - M^2c^2\right\}\phi = 0, \quad . \quad (27a)$$

which is the relativistic form of the Schrödinger equation for a particle.

From (20) and (25) it follows that

$$u.v = \frac{c^2 h\omega}{h\omega - V} = \frac{h\omega}{M}\sqrt{1-v^2/c^2}, \quad . \quad . \qquad (28)$$

in accordance with (18).

§ 7. We now turn to various wave-propagation problems which lead to a dispersion law conforming either to (25) or to (14). Let us begin with equation (25) in the special case for which V is zero throughout.

Then it follows from (25) that

$$u = \frac{c}{\sqrt{1-\frac{M^2c^4}{h^2\omega^2}}}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (29)$$

from which we see at once that our dispersion formula is identical in form with the well-known dispersion law for electromagnetic waves propagated in a medium containing charged particles. Let the number of these particles per c.c. be n, their charge e, and mass m ; then

$$u = \frac{c}{\sqrt{1-\frac{4\pi ne^2}{m\omega^2}}}. \quad . \quad . \quad . \quad . \quad . \qquad (30)$$

It was this accidental coincidence which led Sir J. J. Thomson * to a somewhat obscure interpretation of the interference-phenomena of electron-beams investigated since 1927 by Davisson and Germer, G. P. Thomson, and Rupp.

From (28) it follows that when V = 0

$$u.v = c^2. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (31)$$

§ 8. In the case where the quantity n of § 7 is not a constant, but depends on x, y, and z, the analogy with either formulæ (14) or (25) vanishes.

Now, as this case is specially interesting for some problems concerning the propagation of radio-waves, especially for the questions arising in connexion with the reflexion of these waves by the Heaviside-Kennelly layer, we will indicate in this paragraph a procedure which allows us nevertheless to treat this problem by the methods indicated previously. For this purpose we first show that it is always possible to expand the expression for u in such a way that in a small

* J. J. Thomson, 'Beyond the Electron.' London : Camb. Univ. Press (1928).

interval of frequencies it coincides with formula (14). We write down

$$u=\frac{\omega}{\sqrt{\omega^2/u^2}}=\frac{\omega}{\sqrt{\frac{\omega_0^2}{u_0^2}+2(\omega-\omega_0)\frac{\omega_0}{u_0}\frac{\partial}{\partial u}\left(\frac{\omega}{u}\right)_0}},$$

where u_0 is the value u assumes for $\omega=\omega_0$. It will be possible to bring it in the form (14) if it happens that $2\omega_0/u_0\,.\,\partial/\partial\omega(\omega/u)_0$ proves to be a constant, which may be put equal then to $2M/h$. In this case we have

$$2\frac{\omega_0}{u_0}\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)_0=\frac{2M}{h}, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

$$\frac{2\omega_0^2}{u_0}\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)_0-\frac{\omega_0^2}{u_0^2}=\frac{2M(V+k)}{h^2}, \quad . \quad . \quad (33)$$

$$k+E=h\omega=h\omega_0\,.\,\frac{\omega}{\omega_0}. \quad . \quad . \quad . \quad . \quad (34)$$

Now in our case we have

$$u=\frac{c}{\sqrt{1-\frac{4\pi ne^2}{m\omega^2}}}=\frac{c}{\sqrt{1-N/\omega^2}}, \quad . \quad . \quad (35)$$

where N is written for $4\pi ne^2/m$, and

$$\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)=1:c\sqrt{1-N/\omega^2}\,; \quad . \quad . \quad . \quad . \quad (36)$$

so that

$$\frac{\omega_0}{u_0}\frac{\partial}{\partial\omega}\left(\frac{\omega}{u}\right)_0=\frac{\omega_0}{c^2}$$

proves to be independent of x, y, z.

According to (32), (33), and (34) we have

$$\frac{\omega_0}{c^2}=\frac{M}{h},\quad h\omega_0=Mc^2, \quad . \quad . \quad . \quad . \quad (37)$$

and putting $k=\frac{1}{2}Mc^2$, as is most convenient for our present purpose,

$$V=\frac{Mc^2}{2}\,.\,\frac{N}{\omega_0^2}, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

$$E=Mc^2\,.\,\frac{\omega}{\omega_0}-\tfrac{1}{2}Mc^2=\tfrac{1}{2}Mc^2, \quad . \quad . \quad (39)$$

the difference between ω and ω_0 being neglected in the last expression.

So we see that a group of waves, in the case considered, behaves as a particle of mass M subject to the non-relativistic mechanical law, so that

$$E-V=\tfrac{1}{2}Mv^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

whatever the value of v, if only the potential-field is assumed according to (38).

From (40) it follows that

$$v = c\sqrt{1-N/\omega_0^2}, \quad . \quad . \quad . \quad . \quad . \quad (41)$$

in accordance with (5).

The simplicity of this result suggests that we might have arrived at it in a simpler way. It is, indeed, seen from (35) and (36) that the product of u and v is independent of x, y, z (if $1/v$ is put equal to $\partial/\partial\omega(\omega/u)$); so condition II., § 4, is fulfilled by our dispersion law (30). If we disregard condition I., § 4, it follows immediately from (7) that

$$V = \tfrac{1}{2}Mc^2\frac{N}{\omega^2}$$

if E be chosen arbitrarily equal to $\frac{1}{2}Mc^2$. So, if our sole purpose had been to study formula (30), we could have started here with the omission of §§ 5–8.

§ 9. We now come to the practical problem in which N is proportional to the concentration of the electrons in the Heaviside-layer. Treating first the surface of the earth as flat, we may assume that N only depends on z. Now there exists for a particular frequency ω (the index zero being omitted) a particular value of z ($z(\omega)$ say), for which

$$N(z) = \omega^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

For this value of z V = E. So we see that $z(\omega)$ is the largest value of z that may be reached by the particle whose movement represents that of a group of waves. This value is only reached when the particle starts vertically, *i. e.* when the initial direction of the beam is vertical. In other cases a lower maximal value of z is reached.

After having reached its maximal height, the particle returns to the earth, which means reflexion of the corresponding beam. In many experiments * the time for a group of waves to travel upwards and come down again is measured

* E. V. Appleton and M. A. F. Barnett, 'Nature,' cxv. p. 333 (1925); Proc. Roy. Soc. A, cix. p. 621 (1925), cxiii. p. 450 (1926).
E. V. Appleton and J. A. Ratcliffe, *ibid.* cxv. pp. 291, 305 (1927); cxvii. p. 576 (1927).
G. Breit and M. A. Tuve, Phys. Rev. xxviii. p. 554 (1926).
L. R. Hafstad and M. A. Tuve, Proc. Inst. Rad. Eng. xvii. pp. 1513, 1786 (1929).
G. W. Kenrick and K. C. Jen, *ibid.*, xvii. 711 (1929).
Useful surveys by G. W. Kenrick and G. W. Pickard, Proc. Inst. Rad. Eng. xviii. p. 649 (1930); E. V. Appleton, Proc. Phys. Soc. xli. p. 43 (1928), xlii. p. 321 (1930).

directly or indirectly. This time, of course, will depend on the frequency ω of the group and on the angle θ which the initial direction of the beam makes with the vertical. To avoid duplication of expression let us not speak further of the group, but only of a particle. In case the particle starts vertically, the time needed to travel upwards to its maximal height will be

$$t = \int_0^{(z)\omega} \frac{dz}{\mathrm{V}} = \frac{1}{c}\int_0^{z(\omega)} \frac{dz}{\sqrt{1-\mathrm{N}/\omega^2}}; \quad . \quad . \quad . \quad (42)$$

when starting under an angle θ the velocity will retain a component $c \sin\theta$ parallel to the earth, to which corresponds a portion

$$\tfrac{1}{2}\mathrm{M}c^2 \sin^2\theta$$

of the kinetic energy which remains unaffected.

The particle now will reach a height such that

$$\tfrac{1}{2}\mathrm{M}c^2\cos^2\theta = \mathrm{V} = \tfrac{1}{2}\mathrm{M}c^2\frac{\mathrm{N}}{\omega^2},$$

or

$$\mathrm{N} = \omega^2\cos^2\theta\,;$$

and as

$$\tfrac{1}{2}\mathrm{M}\dot{z}^2 = \tfrac{1}{2}\mathrm{M}c^2\left(\cos^2\theta - \frac{\mathrm{N}}{\omega^2}\right), \quad . \quad . \quad . \quad . \quad (43)$$

$$t = \int\frac{dz}{\dot{z}} = \frac{1}{c\cos\theta}\int_0^{z(\omega\cos\theta)} \frac{dz}{\sqrt{1-\mathrm{N}/\omega^2\cos^2\theta}}, \quad . \quad . \quad (44)$$

so

$$t(\theta,\omega) = \frac{1}{\cos\theta}\, t(0, \omega\cos\theta). \quad . \quad . \quad . \quad (45)$$

So the case $\theta \neq 0$ is reduced to the case $\theta = 0$, and we further need only to consider the latter.

§ 10. The chief problem involved in measurements of this kind is to determine how N depends on the height z when t as a function of ω is determined experimentally. In this case equation (42) is to be considered as an integral equation for N.

Now we may make the formal analogy with a mechanical problem closer in assuming

$$\mathrm{V} = \mathrm{M}.g.y, \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

where $y = \mathrm{N}$ and $g = c^2/2\omega^2$.

Then putting

$$\tfrac{1}{2}\mathrm{M}c^2 = \mathrm{M}.g.a \ (a = \omega^2), \quad . \quad . \quad . \quad . \quad (47)$$

we get

$$v = \sqrt{\frac{2}{\mathrm{M}}(\mathrm{E}-\mathrm{V})} = \sqrt{2g(a-y)},$$

and

$$t(a) = \int_0^{z(a)} \frac{dz}{\sqrt{2g(a-y)}}, \quad . \quad . \quad . \quad . \quad (48)$$

where $z(a)$ means the particular value of z for which $y = a$, so that $t(a)$ is the time a particle starting with velocity c at $z = 0$ needs to travel up a hill $y =$ function (z) * when the gravity-acceleration is chosen so that the maximum height reached is a.

This problem is easily reduced to one of constant gravity-acceleration by multiplying at both sides with

$$2g = c/\omega = c/\sqrt{a}.$$

$$\frac{ct(a)}{\sqrt{a}} = \mathrm{T}(a) = \int_0^{z(a)} \frac{dz}{\sqrt{a-y}}. \quad . \quad . \quad . \quad (49)$$

This is a famous integral equation which was first solved by Abel in 1829 and, in a more elaborated way, by Liouville in 1839. Considering z as a function of y, it reduces to

$$\mathrm{T}(a) = \int_0^a \frac{z'dy}{\sqrt{a-y}}, \quad . \quad . \quad . \quad . \quad . \quad (50)$$

which is a linear equation of the Volterra type. Its solution is

$$z = \frac{1}{\pi}\int_0^a \frac{\mathrm{T}(x)dx}{\sqrt{a-x}}. \quad . \quad . \quad . \quad . \quad . \quad (51)$$

Replacing a by ω^2 and x by ξ^2, we get

$$z = \frac{2c}{\pi}\int_0^\omega \frac{t(\xi)d\xi}{\sqrt{\omega^2-\xi^2}}, \quad . \quad . \quad . \quad . \quad (52a)$$

$$\mathrm{N}(z) = \omega^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (52b)$$

* The z-axis is now thought of as "horizontal," the y-axis as "vertical."

So by formulæ (52) we get z as a function of N instead of N as a function of z.

§ 11. We now consider a number of examples in connexion with equations (42) and (52).

Case 1. Let N be zero throughout. In this case the time for the group to travel from Z_A to Z_B is

$$t(AB) = \frac{1}{c}\int_A^B dz,$$

$$ct(AB) = Z_B - Z_A. \quad . \quad . \quad . \quad . \quad . \quad (53)$$

Case 2. Let N be a linear function of Z,

$$N = a + bz\ ;$$

as N is essentially positive, it will be sufficient to consider positive values of a.
Then

$$ct(AB) = \int_A^B \frac{dz}{\sqrt{1-\frac{a+bz}{\omega^2}}}$$

$$= \frac{1}{\sqrt{1-\frac{a}{\omega^2}}} \int_A^B \frac{dz}{\sqrt{1-\gamma z}} \quad \left(\gamma = \frac{b}{\omega^2 - a}\right).$$

Hence

$$ct(AB) = \frac{2\omega\sqrt{\omega^2-a}}{b}\left[-\sqrt{1-\gamma z}\right]_A^B. \quad . \quad . \quad (54)$$

Let us call $t(AB) = t(\omega)$ if $Z_A = 0$, $Z_B = Z(\omega)$, $N(Z_B) = \omega^2$, so that $\gamma Z_B = 1$.
Then (fig. 1)

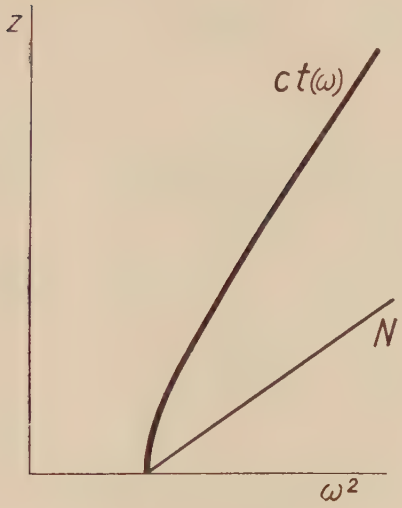
$$ct(\omega) = \frac{2\omega}{b}\sqrt{\omega^2-a}. \quad . \quad . \quad . \quad . \quad . \quad (55)$$

And in the special case that $a = 0$,

$$ct(\omega) = \frac{z\omega^2}{b} = 2z(\omega). \quad . \quad . \quad . \quad . \quad . \quad (56)$$

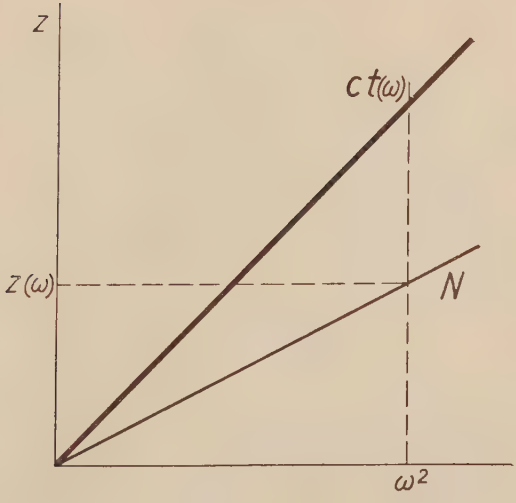
So in this case the time for the group to reach its maximal height is exactly twice the time to travel the same distance *in vacuo* (fig. 2).

Fig. 1.



$$N = a + bz.$$

Fig. 2.



$$N = bz.$$

It is easy in this case to verify formula (52), for

$$\frac{2}{\pi}\int_0^{\omega}\frac{2\xi^2}{b}\frac{d\xi}{\sqrt{\omega^2-\xi^2}}=\frac{4\omega^2}{\pi b}\int_0^1\sin^2\phi\,d\phi=\omega^2/b=z(\omega)$$

$$(\xi=\omega\sin\phi).$$

We need not make the same test in the following cases, as this may be done by simple integration, and involves no particular difficulties.

Case 3. Let N be a quadratic function of z, which is nowhere negative:

$$N=a+pz+qz^2.$$

First, let a, p, and q be positive; then

$$ct(AB)=\int_A^B\frac{dz}{\sqrt{1-\frac{a+pz+qz^2}{\omega^2}}}$$

$$=\omega\int_A^B\frac{dz}{\sqrt{\omega^2-a-pz-qz^2}}$$

$$=\frac{\omega}{\sqrt{q}}\left|\sin^{-1}\frac{2qz+p}{\sqrt{p^2+4q(\omega^2-a)}}\right|_A^B.$$

When especially $Z_A=0$,

$$a+pZ_B+qZ_B^2=\omega^2,\quad Z_B=Z(\omega),$$

$$ct(\omega)=\frac{\pi}{2}\frac{\omega}{\sqrt{q}}\left\{1-\sin^{-1}\frac{p}{\sqrt{p^2+4q(\omega^2-a)}}\right\}. \quad (58)$$

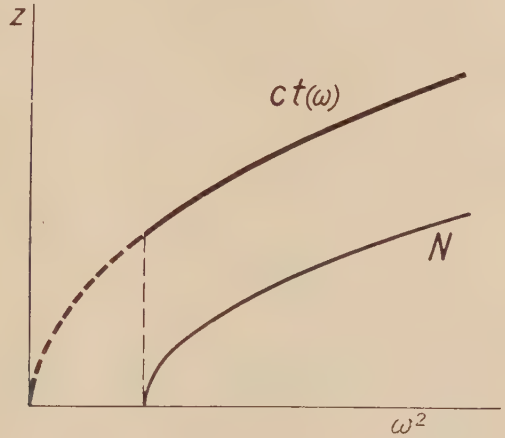
If $p=0$ (fig. 3),

$$ct(\omega)=\frac{\pi}{2}\frac{\omega}{\sqrt{q}}, \quad (59)$$

which, of course, applies only for $\omega^2>a$. If $\omega^2=a$, $z(\omega)=0$, $ct(\omega)=\frac{\pi}{2}\sqrt{\frac{a}{q}}$, so in this case the group requires a finite time for a distance zero, as a result of the group velocity being zero.

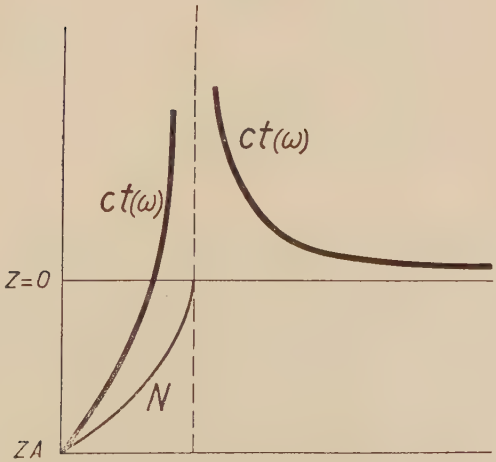
It is remarkable that formula (59) holds independent of the value of a. If $a = 0$, the group-time is exactly $\frac{\pi}{2}$ times the vacuum time.

Fig. 3.



$$N = a + qz^2.$$

Fig. 4.



$$N = a - q'z^2.$$

If q is negative, it is sufficient to consider the case in which $p = 0$ (fig. 4).

Then, if $q' = -q$,

$$ct(\mathrm{AB}) = \frac{\omega}{2\sqrt{q'}} \left| \ln \left| \frac{q'z + \sqrt{q'(\omega^2 - a + q'z^2)}}{q'z - \sqrt{q'(\omega^2 - a + q'z^2)}} \right| \right|_{\mathrm{A}}^{\mathrm{B}}. \quad (60)$$

First, let $\omega^2 < a$. Then, if z_{A} be taken such that $\mathrm{N}(z_{\mathrm{A}}) = a - qz_{\mathrm{A}}^2 = 0$, $\mathrm{N}(\mathrm{Z_B}) = a - qz_{\mathrm{B}}^2 = \omega^2$, $z_{\mathrm{B}} = z(\omega)$, $t(\mathrm{AB}) = t(\omega)$.

$$ct(\omega) = \frac{\omega}{2\sqrt{q'}} \ln \frac{\sqrt{a} + \omega}{\sqrt{a} - \omega} \ldots \quad (61)$$

If $\omega^2 > a$, let $z_{\mathrm{B}} = 0$, $t(\mathrm{AB}) = t(\omega)$.

$$ct(\omega) = \frac{\omega}{2\sqrt{q'}} \ln \frac{\omega + \sqrt{a}}{\omega - \sqrt{a}} \ldots \quad (62)$$

If $\omega^2 \to a$, $ct(\omega) \to \infty$ in both cases.

§ 12. Formula (61) gives an interesting example of a grouptime tending to infinity for a special value of ω. As Professor Appleton has pointed out, in the discussion of his lecture at Eindhoven, this may be of interest in connexion with some particular phenomenon observed since 1928, namely, that of abnormally retarded echoes *.

When (as is suggested by Professor E. V. Appleton) the Heaviside layer consists of two ionized regions (E and F regions) at heights of about 100 and 200 kM, it is possible that the quantity N reaches a maximum for a certain value of z, then a minimum and then increases again, so that to a certain value of N may correspond three values of z. In this case the dependence of $t(\omega)$ on ω^2 may be as depicted in fig. 5.

§ 13. The question arises whether in the case of z being a multivalued function of N it is possible to reconstruct this function from the data available. That this is generally impossible may be shown in the following way. For values of ω^2 superior to N(E) the function $t(\omega)$ may be considered as the sum of $t(\mathrm{OE})$, $t(\mathrm{EF})$, and $t(\mathrm{FP})$, the height of P being $z(\omega)$. From these three parts $t(\mathrm{OE})$ may be deduced

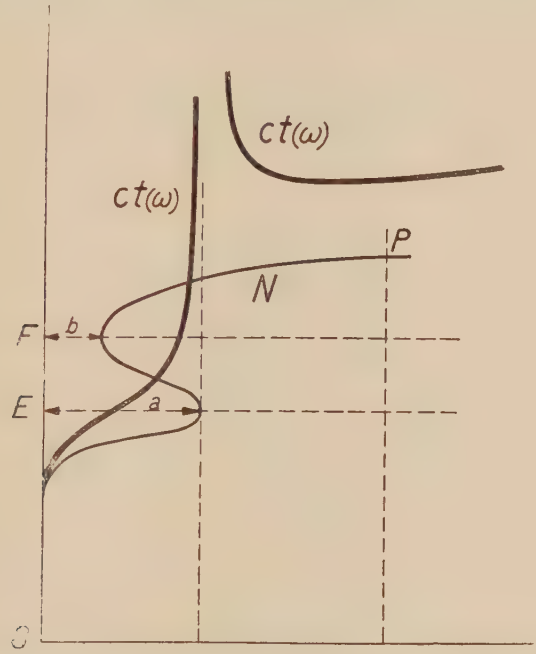
* C. Störmer, 'Nature,' cxxii. pp. 681, 945 (1928).
B. van der Pol, 'Nature,' cxxii. p. 878 (1928), and E. V. Appleton, 'Nature,' cxxii. p. 879 (1928), suggested the idea that this phenomenon might be connected with zero group-velocity; the explanation given by Prof. Störmer is based on widely different assumptions. A general survey of observed facts is given by C. Störmer (*Nat. wiss.* xvii. p. 643 (1929)).

directly from the values of N for $z < z_E$ as found by solving the integral-equation. As may be seen from formula (62) $t(\mathrm{OE})$ will behave as

$$-\log(\omega - \sqrt{a}).\text{const.}$$

for $\omega^2 - a \ll a (a = \mathrm{N(E)})$.

Fig. 5.



Subtracting $t(\mathrm{OE})$ from $t(\omega)$ we retain $t(\mathrm{EF}) + t(\mathrm{FP})$. Of these two functions the latter will behave quite regularly in the neighbourhood of $\omega^2 = a$, while the former becomes infinite as

$$-\log(\omega - \sqrt{a}).\text{const.}$$

probably with the same constant, namely, if N as a function of z behaves as a parabola in the immediate neighbourhood of $z = z(\mathrm{E})$. If $t(\mathrm{EP})$ as a function of ω is accurately known in the region indicated, the constant may be derived experimentally, for

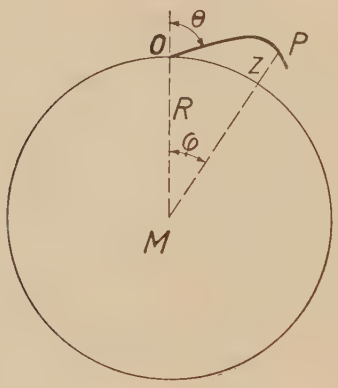
$$\rho^{-ct(\mathrm{EP})}$$

will be proportional to $\omega - \sqrt{a}$.

Now, it will be possible to draw an *arbitrary* curve which has the exact curvature in E and has a minimum in F, the height of F being arbitrary also. Assuming this curve for N between z_E and z_F, it is possible to calculate the corresponding $t(EF)$. Substracting this from $t(EP)$, we retain a function which behaves regularly for $\omega^2 = a$, and we may interpret this function as $t(FP)$. Now, as this function is only fixed for $\omega^2 > a$, we may extrapolate it in quite an arbitrary way for smaller values of ω^2. Then, beginning at F we may construct the curve FP by means of formula (52), so that

$$z_P - z_F = \int_{\sqrt{b}}^{\omega} ct(\xi)d\xi/\sqrt{\omega^2-\xi^2}, \text{ where } t(\xi)=t(PF),\ b=N(F).$$

Fig. 6.



So the result is shown to be dependent on an infinity of voluntary assumptions, and it will be quite impossible to find out the true dependence of N on z in this way. This indeterminedness is already foreshadowed in the example to which formula (59) refers. In this example different functions N give the same $t(\omega)$, so it is impossible to find N(Z) from $t(\omega)$ if the point of beginning is unknown. On the other hand, the assumptions about F and about $t(FP)$ for $\omega > a$ are limited, because $t(FP)$ may not turn out negative, and because a very peculiar form of these curves must be rejected as unnatural. So it may turn out that in practice the function $N(z)$ is to be fixed with a certain degree of probability.

§ 14. It may be shown that the bending of rays round the earth by a spherical layer may be treated by the same methods. In this case (fig. 6) the concentration n, and thus N, depend on the radius vector r. Let the ray be supposed to start at 0 with an angle θ to the vertical. Let

$$\mathrm{MP} = r = \mathrm{R}+z, \quad \mathrm{MO} = \mathrm{R}, \quad \angle \mathrm{OMP} = \phi.$$

Then we have to apply the mechanics of a point moving in a central field of force.

In this case we have

$$\tfrac{1}{2}\mathrm{M}(\dot{r}^2+r^2\dot{\phi}^2)+\mathrm{V} = \mathrm{E}, \quad . \quad . \quad . \quad . \quad (63)$$

where

$$\mathrm{E} = \tfrac{1}{2}\mathrm{M}c^2, \ \mathrm{V} = \tfrac{1}{2}\mathrm{M}c^2\frac{\mathrm{N}}{\omega^2};$$

so

$$\dot{r}^2+r^2\dot{\phi}^2 = \left(1-\frac{\mathrm{N}}{\omega^2}\right)c^2 \quad . \quad . \quad . \quad . \quad . \quad (64)$$

Now, because the field is a central one,

$$r^2\dot{\phi} = \text{const.} = \mathrm{R}c\sin\theta, \quad . \quad . \quad . \quad . \quad (65)$$

so that

$$\dot{r}^2 = c^2\left(1-\frac{\mathrm{N}}{\omega^2}-\frac{\mathrm{R}^2}{r^2}\sin^2\theta\right), \quad . \quad . \quad . \quad (66)$$

Now, as $r-\mathrm{R} = z \ll \mathrm{R}$,

$$1-\frac{\mathrm{R}^2}{r^2} = \frac{2z}{\mathrm{R}}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

thus

$$cdt = -\frac{dr}{\sqrt{\cos^2\theta+\dfrac{2z}{\mathrm{R}}\sin^2\theta-\dfrac{\mathrm{N}}{\omega^2}}}, \quad . \quad . \quad . \quad (68)$$

$$d\phi = \frac{\sin\theta}{\mathrm{R}}\frac{\left(1-\dfrac{2z}{\mathrm{R}}\right)dz}{\sqrt{\cos^2\theta+\dfrac{2z}{\mathrm{R}}\sin^2\theta-\dfrac{\mathrm{N}}{\omega^2}}}. \quad . \quad . \quad (69)$$

From this the time and the place of the point P may be derived by mere integration. In the special case that $\theta = 90^\circ$

$$\mathrm{R}\phi = \int\frac{\left(1-\dfrac{2z}{\mathrm{R}}\right)dz}{\sqrt{\dfrac{2z}{\mathrm{R}}-\dfrac{\mathrm{N}}{\omega^2}}}.$$

The maximal value of z is reached when the denominator is zero. As

$$\frac{2z}{\mathrm{R}}$$

is of the order of magnitude of $\frac{1}{30}$, it is seen that the returning of the wave-group to the earth begins at a point where the concentration is only $\frac{1}{30}$ of the corresponding concentration in the case of vertical ascent.

Further, putting

$$(\mathrm{R}+z_e)\phi = ct,$$

it is possible to calculate the effective height z_e at which the waves have to travel, neglecting dispersion, to arrive in the same time. For $\theta = 90°$ approximately

$$z_e = \frac{\int 2z\, dz/\sqrt{2z/\mathrm{R}-\mathrm{N}/\omega^2}}{\int dz/\sqrt{2z/\mathrm{R}-\mathrm{N}/\omega^2}} \quad . \quad . \quad . \quad . \quad (70)$$

§ 15. In the foregoing paragraphs I have tried to present some results which may be of use to those who work in the field of radio-wave propagation. There are, perhaps, two practical objections to my results which I should like to point out myself: first, absorption is never accounted for *, and in the second place, we always assumed the condition (*b*) § 2 to be valid. Now this condition, translated into the quantities belonging to the mechanical image, becomes

$$(b') - \ldots \frac{h}{\mathrm{M}} \left| \operatorname{grad} \mathrm{V} \right| << (\mathrm{E}-\mathrm{V})^{3/2},$$

so it no longer holds when $\mathrm{E} = \mathrm{V}$. Thus, especially in the case of vertical ascent, something may happen at the maximal height which affects our results. This would require a careful examination of the original wave-equation, containing the time, ω being eliminated.

* P. Epstein (Proc. Nat. Ac. Sc. xvi. p. 37, 1930) recently proved that absorption may have a large influence on the behaviour of the rays.

LII. *Further Experiments on the Cohesion of Quartz Fibres.* *By* G. A. Tomlinson, *B.Sc.* (*from the National Physical Laboratory*) *.

IN a recent paper on "Some Phenomena of the Contact of Solids"† some very interesting experiments were described by Mr. W. Stone, who finds the adhesion of fused glass beads to be due to the presence of a water film on the surface of the glass. The adhesion invariably vanished in an atmosphere of dry air, and reappeared on renewing the film by breathing on the beads.

Mr. Stone made reference to my paper‡ on "Molecular Cohesion," remarking that his experiments lead to somewhat different conclusions. My principal conclusions were based on a study of the adhesion of quartz fibres, and it would certainly be necessary to revise these conclusions considerably if Mr. Stone's explanation of the adhesion of glass beads should apply also to the case of quartz fibres. I gave reasons in the paper for believing that the attraction of the fibres was a case of true cohesion, and was not an electrical force or a surface tension effect, my reason for excluding the latter being that the fibres immediately before an experiment were heated in a flame almost to the softening point of fused silica. The publication of Stone's interesting work, however, made it very advisable to test the adhesion of quartz fibres in a similar way, and a brief account of some further experiments follows.

Two quartz fibres were placed in a thick-walled brass cylinder, attached to metal rods passing through rubber bungs with enough flexibility to allow them to be manipulated from outside, to move them into contact or separate them. The fibres were heated in a flame, and the vessel immediately sealed up with a glass plate at each end. The fibres were now tested, and exhibited their usual property of adhesion. Dried air was then circulated through the vessel, having passed on its way through sulphuric acid, two calcium chloride towers, a tube containing a mixture of phosphorus pentoxide and powdered ignited pumice, and, finally, a cotton-wool

* Communicated by the Author.
† Phil. Mag. ix. p. 610 (1930).
‡ *Loc. cit.* vi. p. 695 (1928).

filter. The air emerging from the vessel was not passed into the atmosphere, but was returned in a closed circuit through the drying system.

The result of this experiment was that I could detect no change in the adhesion of the fibres after circulating the dried air continuously for about six hours. After this the vessel was left in open communication with the drying tubes, and I have examined the adhesion at frequent intervals. Although the present experiments are largely qualitative, the strength of adhesion can be judged fairly well by the elastic deflexion of the fibres, and at the end of seven weeks in a dry atmosphere there was little, if any, diminution in the observed adhesion. On the other hand, fibres left exposed to the atmosphere lose most of their adhesion in a few hours, due to the slow accumulation of contaminating matter from the air.

To verify these results further, I have made another experiment, using two fibres in a different vessel that was exhausted by a mercury condensation pump. At the same time the fibres were heated by means of two grids of nichrome wire wound on mica frames, the fibres being situated between the two grids. This time the fibres were manipulated by deflecting a flexible magnetic needle suitably disposed inside the vessel. After subjecting the fibres to this treatment for the whole of a day, there was no change noticeable in the adhesion. A thermo-couple was afterwards substituted for the fibres, the temperature of which under the same conditions was found to be 140° C., which is probably lower than the corresponding temperature of the fibres owing to the higher thermal conductivity of the metal wires.

My experiments thus show that the adhesion of quartz fibres is not due to a film of water, as Stone found in the case of the glass beads. I find that in a dry and dust-free atmosphere the adhesion of quartz, instead of vanishing, persists for an unprecedented length of time. As regards the adhesion of glass in general, in my earlier experiments the behaviour of glass was found to be very fickle, and for this reason quartz was a preferable material to work with. For example, in working with glass one pair of blown bulbs might exhibit no tendency at all to adhere, like the dried glass beads in Stone's investigation. A different pair, on the other hand, may behave in a

way which leaves little doubt that the surfaces unite in true cohesion. The severance of the two can sometimes actually be heard as a faint musical clink, and the making of contact is frequently audible as a rather harsh rasping sound, probably caused by slight tremors in the tangential direction at the instant of contact.

An experiment I have described elsewhere* may be referred to, as affording independent evidence that this condition of solid cohesion can be realized experimentally. In this experiment a light disk having 3 feet of clean lead is placed on a plate of clean glass (or steel), and the plate is carefully inverted. This can be done leaving the disk clinging to the underside of the plate.

Another experiment, not described hitherto, leads to the same conclusion, and perhaps has some interest in the present connexion. If a clean piece of glass is stroked repeatedly with a clean piece of metal, a faint film gradually forms on the surface of the glass. The first appearance resembles a dirty mark on the glass, but it is impossible to remove the film by hard rubbing or any ordinary mechanical means. On continuing the stroking the film increases in thickness and begins to assume the characteristic colour of the metal used. Its attachment to the glass remains very tenacious, and even hard scraping with the tip of a knife only results in removing the upper layers of the film. The layer in contact with the glass persists after prolonged scraping, although it has been reduced in thickness so far as to lose its characteristic colour altogether and become semi-transparent. Various metals, including copper, aluminium, nickel, lead, iron, and tin can be deposited upon glass in this way, and also upon polished hardened steel. A peculiarity of the film, in the case of a soft metal such as lead, is that when scraping it with a knife it feels considerably harder than the metal would be normally, giving the impression that some of the hardness of the surface layer of the glass is imparted by the bonding forces to the film of metal atoms. There can be little doubt that these films are united to the glass by cohesion bonds comparable in tenacity with those existing in the interior of a solid.

I have mentioned these other undoubted cases of solid cohesion because it is in some respects surprising

* *Loc. cit.* vii. p. 905 (1929).

that cohesive attraction so largely eludes direct observation. The phenomena of solid friction and wear strongly suggest that cohesive combination is always an accompaniment of contact, a view also advocated recently by P. E. Shaw* in connexion with tribo-electric phenomena and friction. It is probably the comparative coarseness of most solid surfaces, when considered in units of atomic dimensions, that renders the cohesive attraction generally imperceptible.

LIII. *A Micromanometer of High Sensitivity.* *By* E. Ower, *A.C.G.I., B.Sc, National Physical Laboratory* †.

OF the various types of instruments yet devised for air speed measurement, undoubtedly the most reliable and satisfactory is the combined pitot-static tube, which forms the accepted standard for speeds of the order of 15 feet per second and upwards. In view of the increased attention paid in recent years to the measurement of low air speeds, it is desirable to extend the calibration and use of the pitot-static tube to much lower speeds. Unfortunately, however, the differential pressures set up at such speeds are so small that considerable difficulty is experienced in measuring them with sufficient accuracy. The lowest speed for which the velocity head can be measured with an accuracy of ± 1 per cent. by the use of the standard 13-inch Chattock gauge is about 6 feet per second; but this degree of precision can only be achieved, at this speed, under the best conditions, and by taking the mean of numerous observations.

Attempts to increase the sensitivity of the Chattock gauge have not met with appreciable success, and the writer has therefore spent much time in a search for a means of measuring pressure differences that shall be capable of considerably greater sensitivity than the Chattock gauge and yet be as simple as possible. In this work he has borne in mind the desirability of the retention of one of the great advantages of the Chattock

* *Loc. cit.* ix. pp. 577, 628 (1930).

† Communicated by E. F. Relf, Superintendent, National Aerodynamics Department.

gauge—that its calibration can be determined purely from measurements of length and of the density of the manometric liquid.

Many different devices were examined before a solution was found, but they all failed to give satisfaction, either on account of their extreme sluggishness of action under very small differential pressures, or because their zero readings were indefinite. Finally, the writer came across references to papers by B. J. P. Roberts * and A. Henry† describing proposals for manometers consisting, in effect, of U-tubes having their two vertical limbs connected by a length of horizontal capillary tubing in which a small air-bubble separates the two columns of liquid. In both cases the applied pressure difference was to be measured in terms of the displacement of the bubble along the capillary tube. An instrument of this type possessing both the necessary sensitivity and a reasonable range would require a capillary of considerable length, and there would be a possibility that the bubble might not return exactly to its zero position after a large movement; the latter effect was, in fact, noticed by Henry. It appeared possible, however, that a null reading instrument based on these lines and using the Chattock principle, in which the movement of the liquid levels under pressure is balanced by tilting the cups, might be successful, and this proved to be the case.

Preliminary experiments with two cups, similar to those ordinarily used in the Chattock gauge, and connected by means of capillary tubing, showed that by a suitable choice of dimensions and manometric liquid an instrument sensitive to pressure differences of the order of 0·00001 inch of water could be designed without difficulty. This sensitivity was attained with the experimental rig-up with cups about 100 mm. diameter and capillary of 3 mm. bore and with xylol as the manometric liquid, and the rate of response to pressure changes was satisfactorily rapid. A number of liquids was tried, but none seemed as good as xylol in respect of mobility of the air-bubble in the capillary. Xylol is suitable also in other ways, as it is not excessively volatile and has a specific gravity less than that of water (about 0·86). Among other facts

* "On a Compensated Micromanometer," Proc. Roy. Soc. **A**, lxxviii. p. 410 (1906).

† "A Micromanometer," *Comptes Rendus*, clv. p. 1078 (1912).

established by these preliminary experiments was the need to maintain steady and uniform temperature conditions over the whole instrument and the necessity for keeping the capillary horizontal. In the latter connexion, it was observed that when the capillary was inclined the bubble drifted under gravity towards the higher end, although the rate of movement was exceedingly slow for small inclinations.

The fact that the bubble can drift in an inclined capillary tube indicates that liquid can pass between its boundaries and the walls of the tube. It might, therefore, be feared that, even if the tube be horizontal, after the bubble has moved under an applied pressure difference it may fail to return to its original zero position upon removal of the pressure. However, this effect was found to be imperceptible ; nor has it been observed under the more refined observations that can be carried out on the finished instrument. In practice, moreover, excessive motion of the bubble will be prevented by the use of a tap as in the Chattock manometer. All that is, in fact, necessary is to ensure that the capillary always remains horizontal irrespective of the movement of the cups. This can be done either by providing flexible rubber connexions between the capillary and the tubes leading from the cups and clamping the capillary to a fixed support, or by arranging the axis of the capillary to be parallel to the axis about which the cups tilt. From the following description of the finished instrument it will be seen that the latter alternative was preferred, as it was thought that difficulties might arise from small volume changes consequent on the movement that would have to be allowed to flexible connexions.

Description of the Instrument. (See figs. 1–3.)

As will have been gathered from the foregoing remarks, the instrument embodies the Chattock tilting principle with, however, a much more sensitive means of indication. In order to maintain the two cups at as nearly the same temperature as possible they are bored out of a single gun-metal casting and have thick walls ; their internal diameter is 4 inches. To the underside of the cup casting are soldered three small steel balls which engage with a cone H, a lateral groove (not shown), and a horizontal

plane K carried by the upper lever D; the plane is provided with vertical screw adjustment. In this way the cups are geometrically located on the lever D, but can be lifted off if required. This lever is hinged to a

Fig. 1.

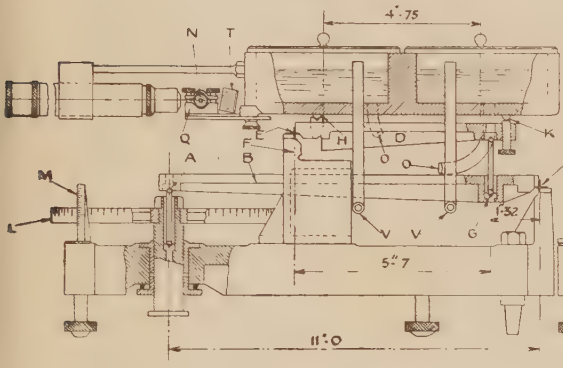


Fig. 2.

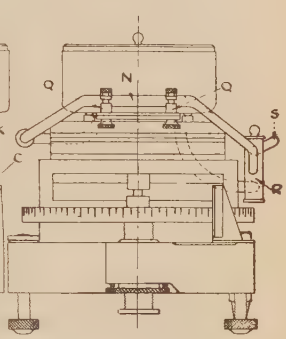
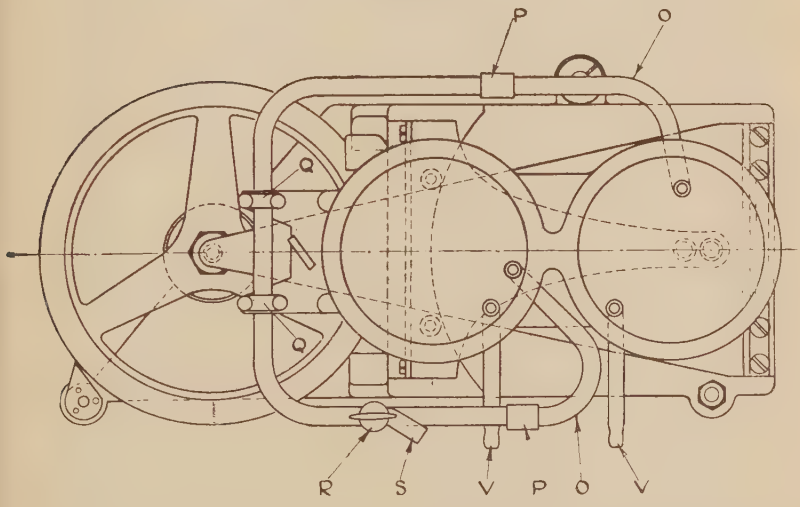


Fig. 3.



bridge piece F, which is securely bolted to the main base casting by means of crossed strips of spring steel, as shown at E, the axis of rotation being the intersection of the horizontal and vertical strips. Frictionless motion

is thus secured. The free end of D carries an inverted conical cup which engages with the upper end of a ball-ended strut whose lower end works in a similar cup G, fixed in the intermediate lever B near the fulcrum of the latter. This intermediate lever is hinged in the same manner to the base casting by spring hinges at C, while its free end A is moved, by means of a ball-ended strut-and-cup arrangement exactly similar to that already described, by the main micrometer screw, which is partially bored out as shown, to accommodate the strut. The micrometer screw works in the base casting which rests on three supports, two of which are adjustable for levelling purposes and are arranged so that the capillary can be levelled without affecting the tilt of the cups.

The function of the intermediate lever between the cup casting and the micrometer screw is to provide a mechanical reduction of the motion of the cups, so that the relative vertical motion of two points, one on each cup axis, is only 1/10 of the corresponding movement of the screw. How this is effected will be clear from the figures. Thus it is possible to ensure that, as far as the mechanical construction of the instrument is concerned, readings can be repeated to the desired degree of accuracy, viz., 0·00001 inch, without demanding a screw thread cut to limits outside those possible with normal workmanship.

The motion of the cups is read by means of the graduated rim of the wheel L attached to the micrometer screw and moving over the fixed vertical scale M. Slightly over an inch of total travel is permitted for the screw, whose buttress thread has a pitch of 0·05 inch. The diameter of the screw is 1 inch, and a spring nut is provided to prevent possible back-lash. The periphery of the wheel is divided into 500 parts, each of which represents 0·00001 inch change of liquid level in the cups, and is actually rather more than 0·04 inch long.

The capillary tube N forms part of a circuit of tubing (not shown completely in fig. 1; best seen in fig. 3) providing free communication between the liquid in the two cups. Of this circuit the parts OO soldered to the cups consist of "compo" tubing of about $\frac{1}{4}$-inch bore leading to lengths of glass tubing of the same bore. The capillary tube, of 3 mm. bore and about 3 inch long, is fixed at each end of these portions of glass tube. Connexion between the latter and the compo tubes is made

by means of corks PP impregnated with gelatine solution to render them leak-tight. Rubber joints are precluded, as they are soon destroyed by the xylol. The compo tubing, while being amply stiff, still has sufficient flexibility to enable it to be bent with ease, so that its ends butt accurately in line against the ends of the glass tubes to which it is connected. Undue strains on the glass-work, which is independently held by rigid clamps, are thus avoided when the corks are in place. The horizontal capillary forms the highest part of the tubing circuit, so that there is no risk of loss of the bubble. The capillary is gripped in two V-blocks QQ carried by a brass plate supported from the cup casting and provided with a certain amount of adjustment, so that the axis of the capillary can be set horizontal and parallel to the axis of tilt of the cups.

Once in the glass tube the air-bubble rises into the capillary. The bubble is easily introduced through the two-way tap R, by means of which one of the cups can be connected either to the other cup or to a short open-ended branch tube S. After all the tubing connecting the cups has been filled with liquid the tap is turned so as to connect one of the cups with the open branch, and the bubble is forced in under a small head of liquid. A further function of the tap, which is performed by means of a quarter turn, is to stop all movement of the bubble as in the Chattock gauge.

The bubble is viewed through a microscope of about 30 magnifying power, carried by a bracket from the cup casting, and is illuminated by light reflected from the small adjustable mirror T. As source an ordinary 4-volt flash-lamp bulb is used, which at first was carried by a bracket from the microscope holder, but in this position, although the filament was over 2 inches from the capillary and above it, the minute quantity of radiant heat reaching the capillary was sufficient to disturb the zero reading seriously each time the bubble was allowed to move. The lamp is now fixed to the outside of the temperature insulation box in which the manometer is enclosed. Light from the lamp passes through a glass cell let into the wall of the box, and containing a solution of cupric chloride to filter the heat rays. The box itself is of wood, double-walled, with broken cork packing in the wall space, and lined with copper sheet. The microscope passes

through a hole in the front wall, while a claw projects through the roof for operation of the tap R. A universal joint is included in the claw spindle, and the claw is fairly slack on the head of the tap, so that the main action applied by the claw is a torque with little bending. Of the manometer itself only the front of the rim of the graduated micrometer wheel protrudes from the box, the necessary aperture being covered by a velvet curtain. Even so, it is essential to lag the capillary tube with cotton wool, to screen it from the heat of the hand of the operator adjusting the wheel.

Copper tubes VV, passing up through the bottoms of the cups and projecting above the levels of the liquid, serve to connect the instrument to the sources of pressure whose difference is to be measured. The cups are sealed by means of glass desiccator lids with ground rims resting on the tops of the cup walls, which are machined and polished. The joints are made good in the ordinary manner, except that instead of grease, which is attacked by xylol, soft soap is used. A viscous mixture of treacle and glycerine is used as a lubricant for the two-way tap.

With the somewhat extensive protection against temperature changes described, the performance of the instrument is entirely satisfactory, and it responds quite readily to changes of the applied pressure difference. The total vertical range of the cup movement is just over 0·1 inch, so that velocity heads corresponding to air speeds from 20 feet per second downwards can be measured. On the assumption of a sensitivity of 0·00001 inch of water, the lowest velocity head that can be measured to one per cent. accuracy corresponds to a speed of 2·1 feet per second. Actually, the sensitivity of the instrument is better than this: it is possible over short intervals of time (two or three minutes) to repeat the zero reading to at least 0·000005 inch. But whether conditions will remain steady long enough for this accuracy always to be achieved in practice is doubtful. Certain measurements already made of the differential pressure set up by a pitot-static tube moving through air at about 1·6 feet per second indicate that generally the zero for a single reading will not be certain to finer limits than 0·00001 inch. By taking the mean of several readings, however, the accuracy can probably be improved somewhat. It is, then, safe to say that the manometer is capable of

measuring the velocity head for a speed of 2 feet per second with an accuracy of ± 1 per cent., and that, under favourable conditions, this accuracy can be extended to a somewhat lower speed. On speed itself the accuracy is, of course, double that on velocity head ; so that, provided a reliable source of velocity head is available, a speed of about 1·5 feet per second can be measured to ± 1 per cent.

It should be pointed out that no claim is advanced that this instrument is suitable for the measurement of low air speeds in mines or engineering works, although in certain conditions it may be possible to use it for such purposes. The accurate measurement of low speeds is a difficult operation which is best carried out in the laboratory. This manometer is intended to be chiefly a laboratory standard against which other instruments, such as vane, torsion, or hot-wire anemometers, better adapted for general use, can be calibrated.

Valuable advice was given during the design of the instrument by Dr. G. Barr, of the Chemistry Department, N.P.L., in connexion with the chemical problems that arose, and by Mr. J. E. Sears, Jr., of the Metrology Department, on certain important mechanical details ; and the writer wishes to express his indebtedness to both these gentlemen.

LIV. *Crystal Structure in the System Copper-Bismuth.*

By William F. Ehret, *Ph.D., and* Ray D. Fine, *M.Sc.**

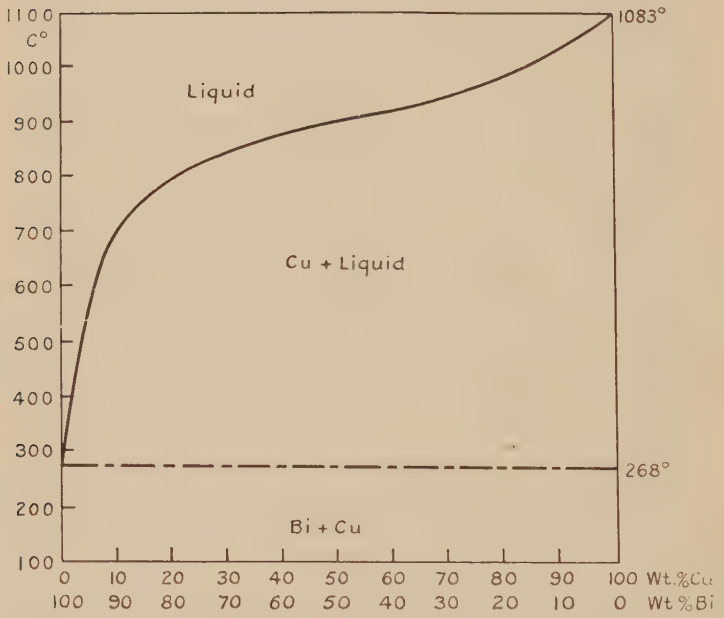
[Plate II.]

CRYSTAL structure in the system Cu–Bi was determined in connexion with a plan to study the relation between structure and composition in systems of the type A–B, in which A is Cu, Ag, or Au and B is As, Sb, Bi, or P. Since this work was begun the results of a crystal-structure analysis of the systems Cu–Sb and Ag–Sb have been published by Westgren, Hägg, and Eriksson [1]. The preliminary results obtained in our laboratory on the alloys of Cu and Sb were in complete accord with those of the Swedish workers, and nothing further has been done with this system. We hope to report our findings in some of the other systems shortly.

* Communicated by the Authors.

The earliest systematic investigation of the alloys of Cu and Bi was probably that by Roland-Gosselin [2]. This and the work of later investigators—Heycock and Neville [3], Gautier [4] and Jeriomin [5]—established the thermal diagram for the system (fig. 1). It is one of the simplest possible, no compound formation or solid solution being indicated. The eutectic temperature apparently lies very close to the melting-point of pure Bi. This in itself is an indication of very low solubility of Cu in liquid Bi at its melting-point. Tammann [6]

Fig. 1.



Equilibrium Diagram of the System Cu–Bi according to Jeriomin.

mentions this system as one of the very few binary metallic systems in which, as far as thermal analysis can discern, no solid solution or compound formation takes place.

For several reasons it might be suspected that the equilibrium diagram is not as simple as the thermal analysis indicates. They are as follows :—(i.) Sb and Bi are known to form a continuous series of solid solutions. The Cu–Sb system [1] involves both solid solution and compound formation. Likewise Cu and Ag form a broken series of solid solutions, and

solid Ag dissolves Bi to the extent of 5·3 per cent.* Also, Au and Cu form an unbroken series of solid solutions and Au dissolves 4·5 per cent. Bi [7]. These facts readily lead to the inference of an appreciable solubility of Bi in Cu. (ii.) In all the systems mentioned above there is appreciable solubility of the lower melting in the higher melting solid †. (iii.) Bernal [8] places Cu fourth on his approximate scale of dissolving power of the metals. On the average, only Pd, Pt, and Ag show greater dissolving power. (iv.) Although it might be argued that solid solution is not to be expected between two metals so different in atomic volume as Cu (=11·8) and Bi (=34·0 c.c. $\times 10^{-24}$) [9], it is well known that Bi is soluble in Ni in the solid state to the extent of 5·0 per cent. even though the atomic volumes of the latter elements show a greater divergence than Cu and Bi.

Several investigations of the solubility of Bi in Cu have been carried out. Jeriomin [5], using the microscopic method, placed the solubility between 0·25 and 0·5 per cent. Portevin [10] found Bi insoluble. Recently, Hanson and Ford [11] concluded, from microscopic observations, that the solubility is approximately 0·001 per cent. Bernal [8] reports the solubility as nil. The deleterious effect of small quantities of Bi upon the rolling properties of Cu, a fact well known to metal workers, points to a very limited solubility of Bi in Cu. This particular phase of the subject has been discussed in several publications recently [12].

Due to certain limitations inherent in the method of X-ray analysis employed, it is only possible to say, as the result of the work described below, that the solid solubility of Bi in Cu, and *vice versa*, is less than approximately 0·5 atomic per cent. Between these limits Cu and Bi form a series of heterogeneous alloys, the characteristic diffraction pattern of both metals being present on all the X-ray photograms.

Preparation and Composition of Alloys.

A series of alloys, covering the whole range, was prepared from electrolytic Cu and from Bi of a high degree of purity supplied by Eimer and Amend, of New York City. Cu was determined electrolytically and Bi by the oxychloride method, after the basic nitrate and the phosphate methods had been

* From results, soon to be published, obtained by S. J. Broderick in this laboratory.

† With the exception of Au–Sb. No information is available concerning the equilibrium diagrams of Au–P and Ag–P.

tried and found less reliable. The compositions were as follows :—

TABLE I.

Sample No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Per cent. Bi ..	0·0	8·0	15·4	23·7	28·6	48·4	60·8	62·0	86·8	93·1	95·5	100
Per cent. Cu...	100	92·0	84·6	76·3	71·4	51·6	39·2	38·0	13·2	6·9	4·5	0·0

The melts were made in unglazed porcelain crucibles in an electrically heated furnace. The temperature was controlled with the aid of a previously determined temperature-current curve for the furnace. The melting was carried on under a thin layer of powdered charcoal and in an atmosphere of illuminating gas. It is believed that oxygen was thus effectively excluded. The melts were cooled rapidly, and samples for X-ray analysis taken by filing. The filings were annealed to remove stains set up during the cooling and cold working. Microscopic examination revealed all alloys heterogeneous and a complete absence of Cu_2O.

Method of Working.

Powder photograms of the pure metals and alloys were taken on the standard Davey apparatus[13]. The diffraction pattern of pure NaCl was taken simultaneously with each of the metal powders, the latter being diluted with corn-starch to reduce their absorptivity to that of the standardizing substance. In order to measure the positions of the diffraction lines accurately, a correction curve, using the known interplanar spacings for NaCl, was drawn for each photogram. The error in the measurements is thereby reduced to about 0·1 per cent. To arrive at the most probable value of the edge-length of the unit cells, the method of plotting the calculated values of log a_0 on arithmetic probability paper[14] was chosen. The mean error of the parameter values given may be estimated at 0·004 Å.

Experimental Results.

Pure Cu.—A large number of determinations of a_0 for the face-centred unit cube of Cu are now available. It may be well to survey the field before giving the results of the present investigation. It is interesting to note that values as

diverse as 3·59 and 3·68 Å. have been reported. Wyckoff [15] summarizes the work previous to 1926 and gives an average value of 3·60(3) Å. Jung [16], in the same year, summarizes the previous work and obtains an average of about 3·60(6) Å., although his own experiments lead to a value of 3·620 Å. Since 1926 a number of careful redeterminations of a_0 for Cu have been made, chiefly in the laboratory of Professor Westgren at Stockholm. They leave little doubt that the most probable value is $3{\cdot}608 \pm 0{\cdot}003$ Å.

In Table II. the results of the present investigation are given. The values of the interplanar distances are, in the case of pure Cu, the averages of readings taken from two photograms.

TABLE II.

Indices of planes.	Cu, d_{hkl}.	Cu, $\log a_0$.	Cu, a_0.	No. 2, d_{hkl}.	No. 2, $\log a_0$.	No. 2, a_0.
111	2·081 Å.	·5567	3·603 Å.	2·081 Å.	·5567	3·603 Å.
100(2)	1·089	·5585	3·618	1·806	·5577	3·612
110(2)	1·281	·5589	3·622	1·282	·5594	3·626
113	1·087	·5570	3·606	1·086	·5566	3·603
111(2)	1·039	·5561	3·598	1·039	·5561	3·598
133	0·828	·5575	3·610	0·829	·5580	3·614
120(2)	0·805	·5566	3·603	0·806	·5568	3·604
	$a_0 = 3{\cdot}607$ Å.			$a_0 = 3{\cdot}604$ Å.		

The most probable value of a_0 for pure Cu as obtained by plotting $\log a_0$ on probability paper is 3·607 Å. If the average of the values of a_0 is taken we get 3·608 Å. The density of Cu, calculated from the foregoing, is 8·94 as compared with the experimental value 8·89 (International Critical Tables). The value of a_0 as obtained from the diffraction lines due to Cu in photograms of alloy No. 2 (Table I.) is 3·604 Å. If the average is taken in this case, we get 3·608 Å. These variations lie within the limits of experimental error, and indicate that any distortion in the lattice of Cu, due to dissolved Bi, is beyond detection by our method. In order to verify the foregoing statement, and at the same time eliminate any errors that might be due to differences in absorptivity, readings taken from two different films, etc., a comparison photogram was made in which the diffraction patterns of Cu and alloy No. 2 were recorded side by side on the same film and under

identical conditions. The average difference between the radii of corresponding diffraction rings on the two spectra is 0·1 per cent. This is the same as the average difference between two sets of measurements of the same spectrum taken at two different times. The two spectra are therefore identical within these limits.

In accordance with what was to be expected, as the result of the microscopic examination, all the alloys produce two superimposed diffraction patterns analogous to Cu and Bi. Pl. II., in which an attempt has been made to reproduce the photograms, shows the parent patterns in each of the alloys.

Pure Bi.—In so far as the authors are aware, no new values for the lattice constants of Bi have appeared since the summary of previous values by Wyckoff in 1926[15]. The parameter values depend upon the axes of reference chosen. When rhombohedral axes mutually inclined at 87°34′ are employed, the average of previously obtained values is 6·549 Å. for the length of the side of the unit rhombohedron containing 8 atoms. With this choice of axes the unit of structure contains two interpenetrating face-centred rhombohedral lattices so situated with respect to one another that the whole lattice appears to be one of slightly distorted simple cubes. If the simpler primitive rhombohedron containing two Bi atoms is chosen as the elementary cell, the axes are mutually inclined at 57° 16′, and the average of previous values of the edge of the elementary rhombohedron is 4·731 Å. Davey[17] used hexagonal axes of reference, and obtained $4{\cdot}539 \pm 0{\cdot}005$ Å. for the side of the elementary triangular prism, the axial ratio being 2·606.

Table III. summarizes the results of our measurements on pure Bi and the corresponding diffraction lines of alloy No. 8. They are based on the simple primitive rhombohedron containing two atoms in the unit cell.

The appended values for a_1 were obtained by the method of graphical solution from the values calculated for the various planes. If averages had been taken, the corresponding values would have been 4·749 and 4·757 Å. respectively. Similar measurements of the photogram for alloy No. 9 give a value of a_1 identical with that of alloy No. 8. Since the difference between a_1 for pure Bi and that for Bi supposedly saturated with Cu is just beyond the limits of experimental error, it is not possible to conclude from these measurements that any solid solution with consequent change in lattice has occurred. This opinion is further supported by one of our photograms in which the diffraction patterns of Bi and alloy

No. 11 were recorded simultaneously and under identical conditions. Measurements of the radii of the diffraction rings due to Bi on the two spectra agreed with one another to within 0·1 per cent.

In order to facilitate comparison of our results with former ones sometimes calculated on the basis of different axes, Table IV. has been constructed. The axial ratio has been established both crystallographically and by X-ray analysis.

Table III.

Indices of planes (87° 34′).	Indices of planes (57° 16′).	Bi, d_{hkl}.	Bi, log a_1.	Bi, a_1 (57° 16′).	No. 8, d_{hkl}.	No. 8, log a_1.	No. 8, a_1 (57° 16′).
200	110	3·29 Å.	·6775	4·759 Å	3·33 Å)	(·6827)	(4·817 Å.)
220	211	(2·354)	(·6737)	(4·718)	2·372	·6770	4·753
$20\bar{2}$	$10\bar{1}$	2·274	·6763	4·745	2·283	·6780	4·764
$22\bar{2}$	222	—	—	—	1·973	·6756	4·738
$22\bar{2}$	200	1·870	·6765	4·748	1·873	·6772	4·755
200	220	1·637	·6754	4·736	1·647	·6780	4·764
420	321	1·495	·6774	4·758	1·496	·6777	4·761
$40\bar{2}$	$21\bar{1}$	1·445	·6767	4·750	1·447	·6773	4·757
$42\bar{2}$	310	1·332	·6768	4·751	1·336	·6781	4·765
		a_1=4·749 Å.				a_1=4·758 Å.	

Table IV.

System of axes chosen.	(Bi) a.	Axial ratio.
Rhombohedral, α=87° 34′	6·577 A.	—
Rhombohedral, α=57° 16′	4·749	—
Hexagonal	4·551	2·606

The intensities of the reflexions for Bi are in agreement with those previously observed[18]. No new light is shed on the question of the amount of displacement of the two face-centred rhombohedral lattices in the direction of the trigonal axis. The calculated density of Bi is 9·72 as compared with the experimental which is 9·67 (International Critical Tables). Our value of a_1 is higher than any previously reported. It corresponds closely to that found by Hassel and Mark[19], viz. 4·74 Å.

There remains to be considered the question of the amount of solid solubility that can be detected by our method. If we make the simplifying assumptions that the atomic radii are equal to one-half the distance of closest approach of the atoms, and that the distance of closest approach is a linear function of the composition, it is possible to calculate, on the basis of the structures of Cu and Bi, that solid solution to the extent of approximately 0·5 atomic per cent. should be detectable. Very little importance can, however, be attached to this estimate, since we are dealing with two different types of structure, and also, as is well known, solid solution frequently occurs without change in lattice.

Summary.

As part of a programme to determine crystal structure in binary alloys in which one component is Cu, Ag, or Au and the other As, Sb, Bi, or P, the structure of alloys of Cu and Bi was examined and is here reported.

All the alloys examined were heterogeneous, showing clearly the superimposed diffraction patterns of Cu and Bi. Within the limits of our experimental error the lattices of Cu and Bi remain unchanged in their alloys. This is indicative of a very low mutual solubility.

The lattice constant of the face-centred unit cube of Cu is redetermined, $a_0 = 3{\cdot}607 \pm 0{\cdot}004$ Å. This is in very close agreement with several recent determinations.

Employing rhombohedral axes, mutually inclined at 57° 16′, the length of the edge of the elementary rhombohedron of the Bi structure is found to be $4{\cdot}749 \pm 0{\cdot}005$ Å. This is slightly higher than previously determined values.

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LV. *The Interaction of Molecules with the Silver Ion**. *By* Frederick Karl Victor Koch†.

IT has been shown by Fajans and Joos (*Zeit. Physik*, xxiii. p. 1. 1924) both on the basis of refractometric data and on theoretical grounds that ions cannot be adequately represented as rigid electronic structures, but that they undergo a certain degree of polarization or "deformation" (Fajans) when subjected to the electrical fields of other neighbouring ions. That such a deformation takes place has been confirmed experimentally both for the crystalline state (Fajans and Joos, *l. c.*) and for concentrated electrolyte solutions in water (Fajans, Kohner, and Geffcken, *Z. Electrochem.* xxxiv. p. 1, 1928). On these lines Fajans (*Z. Elektrochem.* xxxiv. p. 502, 1928) has concluded that the transition from an electrovalent to a covalent linkage is continuous, and that the covalent bond may be regarded as having its origin in the extreme mutual deformation of the electron orbits of the constituent ions.

A parallelism to the above may be predicted for the interaction of ions and molecules, and solvation (the ionic molecular electrovalency) may be regarded as merging gradually into complex formation (the ionic-molecular covalency).

It is therefore to be expected that the refraction of an ion will vary with the solvent in a manner analogous to that with which it varies in the proximity of other neighbouring ions. The refractometric data relating to electrolytes in non-aqueous solvents (see Walden, 'Elektrochemie

* Communicated by Prof. J. C. Philip.
† Beit Scientific Research Fellow.

nichtwässerige Lösungen,' 1924, p. 276) are, unfortunately, so scanty, and the effects to be expected in general are so small, that practically no conclusions can be drawn from this source. Schreiner (*Z. Physikal. Chem.* cxxxv. p. 461, 1928) did, however, find a change in the refraction (extrapolated to infinite dilution) of completely ionized hydrogen chloride and lithium chloride in water, methyl alcohol, and ethyl alcohol which must be ascribed to the effect of the solvent. The refractometric method has the inevitable disadvantage that the data always refer to at least two ions, and thus complicate the interpretation thereof.

Another possible line of approach, which is that attempted in this instance, is to compare the free energies of solvation of an ion which have been determined experimentally (A_E) with those (A_T) calculated by the method of Born (*Zeit. f. Physik*, i. p. 45, 1920) for the *ideal* case on the assumption that the ion is a rigid sphere located in a continuous medium of dielectric constant (ϵ). The differences $A_C = A_E - A_T$ will represent the extra energy expended in the excess mutual deformation above that due to the induced moment (which is taken into account by the dielectric constant). This energy may therefore be termed the "Free Energy of Complex Formation" * (A_C). The experimental values of the free energies (A_E) can be obtained from electrometric measurements of the variation of the electrode potential with the solvent.

The electrode potential of a metal represents the difference in the free energy of the ions in the metallic crystal and in the solvated state. The difference between the normal potential of a metal in two different solvents will therefore represent the difference in the free energies of solvation of the ion (ΔA_E). Thus

$$\Delta A_E = (A_E)_1 - (A_E)_2 = n \,.\, F \,.\, (E_1 - E_2) - R \,.\, T \,.\, \log_e P_1/P_2$$

$$= R \,.\, T \,.\, \log_e \gamma_s,$$ where $(A_E)_1$, $(A_E)_2$ are the free energies of solvation, E_1, E_2 the normal potentials, P_1, P_2 the Nernst solution tensions in the solvents 1 and 2 respectively, and γ_s is the specific distribution coefficient of the metal ion. The values of E_1, E_2, P_1/P_2, or γ_s can be determined experimentally, and hence ΔA_E can be calculated. The

* Under "complex formation" are grouped all those effects which deviate from the ideal state of Born, *e. g.*, (1) change in radius or shape of the ion or surrounding molecules, (2) electrical saturation effects in the medium surrounding the ion.

absolute free energy of solvation (A_E) cannot be determined experimentally. By choosing A_E for a single solvent such that $A_E = A_T$ it is, however, possible to calculate the remaining values of A_E by adding the differences ΔA_E. This procedure will, of course, introduce a constant error into the values of A_E, since it is improbable that the ideal conditions are attained in any actual case. Thus the free energies of complex formation will all be too small by a constant amount (χ), and may more exactly be represented by $(A_C - \chi)$.

The free energies of solvation (A_E) have been calculated for the silver ion in ten organic liquids from the experimental values of P_1 P_2 determined by the author (J. Chem. Soc. 1928, p. 279). The assumption that $A_E = A_T$ has been made in the case of acetone because the solution tension of silver and the solubility of silver nitrate are less in this than in any of the other solvents, and there is therefore reason to suppose that the tendency of the silver ion to form complexes is least in this case.

The ideal free energy of solvation (A_T) of an ion, which represents the work obtained in transfering it from a vacuum into the solvent (ϵ), is given by the formula

$$A_T = 1{\cdot}194 \times 10^{-11} \,.\, e^2 \,.\, z^2 \,.\, N \,.\, (1 - 1/\epsilon)/r_i \text{ kil. calories},$$

where $e = 4{\cdot}774 \times 10^{-10}$ e.s.u. is the electronic charge, z is the valency, and r_i the radius of the ion, and $N = 6{\cdot}06 \times 10^{23}$ is the Avagadro Number. Using the experimental value of $r_i = 1{\cdot}13$ Å.U. given by Goldschmidt (Trans. Faraday Soc. xxv. p. 282, 1929) deduced from X-ray analysis of crystal structure, the above equation reduces to

$$A_T = 146(1 - 1/\epsilon).$$

Uncertainty due to r_i.—The theoretical value for the radius of the silver ion calculated by Pauling (see Goldschmidt, *l.c.*) on the basis of the wave mechanics is $r_i' = 1{\cdot}26$ Å.U., and the value of the radius of the silver atom is $r_a = 1{\cdot}44$ Å.U. The corresponding values of $(A_C - \chi)$ are included in the table in order to illustrate the effect which an error in r_i would have upon $(A_C - \chi)$. An error in r_i would, of course, cause an error in A_T, and hence part of $(A_C - \chi)$ would not be due to a deviation from the ideal state, but to the use of an incorrect ionic radius. The error due to this cause may be estimated as follows :—

$$A_C - \chi = A_E - A_T = A_E - 165 \times 10^{-8}(1 - 1/\epsilon) r_i.$$

By partial differentiation with respect to r_i

$$\partial A_C = 165 \times 10^{-8}(1-1/\epsilon) \cdot \partial r_i / r_i^2.$$

This is the absolute error for all solvents. For acetone ($\varepsilon = 21$) $(A_C - \chi)$ has, however, been taken arbitrarily as zero, and hence the absolute error also becomes zero. The error, referred to zero error for acetone, is therefore

$$\partial A_C' = 165 \times 10^{-8}(1/21 - 1/\epsilon) \cdot \partial r / r^2.$$

Taking $r_i = 1{\cdot}13$ Å.U. and $\partial r_i = \pm 0{\cdot}3$ Å.U., *i. e.*, a 30 per cent. error in the ionic radius—

For aniline.....	$\varepsilon = 6{\cdot}9$	$\partial A_C = \pm 3{\cdot}8$
,, water	$\varepsilon = 81{\cdot}7$	,, $= \pm 1{\cdot}4$
,, acetonitrile	$\varepsilon = 36{\cdot}4$	,, $= \pm 0{\cdot}8$

Uncertainty due to ϵ.—The effect which an experimental error in the dielectric constant would have upon $(A_C - \chi)$ may be found by partial differentiation with respect to ε. Taking $r_i = 1{\cdot}13$ Å.U.,

$$\partial A_C = 146 \cdot \partial \epsilon / \epsilon^2.$$

Nitrogen Bases.

Solvent.	ϵ.	A_E.	A_T.	$A_C - \chi$. $r_i = 1{\cdot}13$ Å.U. (Goldschmidt).	$r_i' = 1{\cdot}26$ Å.U. (Pauling).	$r_a = 1{\cdot}44$ A.U. (atom).
Aniline	6·85	147·2	124·6	22·6	21·1	19·5
Pyridine	12·4	151·7	134·2	17·5	17·1	16·5
Nitriles.						
Phenylaceto-nitrile.....	15	142·8	136·2	6·6	6·6	6·0
Acetonitrile	36·4	145·8	142·0	3·8	3·8	4·5
Propionitrile.....	27·5	144·1	140·7	3·4	3·7	3·8
Benzonitrile	26·3	142·7	140·4	2·3	2·5	2·7
Ethylcyano-acetate	27·7	142·8	140·6	2·2	2·4	2·5
Alcohols.						
Water	81·7	144·0	144·2	(−0·2)	0·4	1·0
Methyl Alcohol	35·4	141·5	141·8	(−0·3)	(−1·3)	(−2·3)
Ethyl Alcohol....	25·4	141·1	140·3	0·8	0·4	1·2
Acetone.....	21	(139·0)	139·0	0	0	0

For an error of 10 per cent. in the dielectric constant—

For aniline	$\varepsilon = 6{\cdot}9$	$\partial\varepsilon = \pm 0{\cdot}7$	$\partial A_c = \pm 0{\cdot}21$
,, water.....	$\varepsilon = 81{\cdot}7$	,, $= \pm 8{\cdot}0$	,, $= \pm 0{\cdot}17$
,, acetonitrile .	$\varepsilon = 36{\cdot}4$	,, $= \pm 4{\cdot}0$	,, $= \pm 0{\cdot}44$

It will be seen that none of these errors is sufficiently large to account for the observed regularities.

The values of $(A_c - \chi)$ fall into three classes, which merge, however, into one another, showing that the transition from solvation to complex formation is gradual. The classification into (1) nitrogen bases, (2) nitriles, (3) alcohols is, moreover, independent of whether r_i, r_i' or r_a be used, but the value $r_i = 1{\cdot}13$ Å.U. must, of course, be regarded as the most appropriate. It therefore appears that these differences have a real significance, and in fact they stand in good agreement with the well-known chemical properties of the silver ion. Complex ions of the type $Ag(C_5H_5N)_2^+$ etc. are known to exist, whereas the silver ion is not known to form definite complexes with water, the alcohols, or acetone. It might perhaps be concluded that the constant error (χ) is negligibly small. The increased activity of the nitrile group in phenylacetonitrile, due to the substitution of the phenyl group in acetonitrile, is paralleled by the author's observation that boiling phenylacetonitrile reacts with silver nitrate, giving silver cyanide, whereas acetonitrile does not. The results thus lend additional support to the above procedure.

Solvation may be defined as that state of ionic-molecular interaction in which the electronic configurations of the ions and molecules are quasi-rigid. In this ideal state the whole deformation effect may be ascribed to the moment induced in a continuous dielectric medium by a rigid ion, and is given by the Born formula (*l. c.*). In any natural case there is, however, a further deformation due to the change in shape of the ion and one or more orientated solvent molecules. In the most extreme cases, which are generally known as " complex formation," the changes are of a still more profound nature, as is evidenced by the well-known colour effects etc., and there is an exact stoichiometrical relationship between the constituent ions and molecules. It is further to be expected that the action of the ion will be localized at certain parts of the molecules, and in the above examples of the silver ion at the nitrogen

and oxygen atoms. Since the refraction of an electrical system is a measure of its deformability (*cf.* Debye, *Handb. der Radiologie*, Bd. vi. p. 605), it is of interest to note that the refraction of nitrogen in aniline (primary amine) is 2·32 of nitrogen in pyridine (mol. refract. pyridine—5/6 mol. refract. benzene) is 2·25 ; of nitrogen in the nitriles (including half the acetylene bond) is 1·92 ; of oxygen in hydroxyl 1·52 ; and of oxygen in ketones 1·62.

In conclusion, the author wishes to thank the Trustees of the Beit Fellowship for a Fellowship.

Physical Chemistry Department,
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London, S. W. 7.
19th May, 1930.

LVI. *A Theorem in Determinants.* *By* J. B. Coleman *.

THEOREM.—If the signs of all the elements in the alternate diagonals of a determinant be changed, the value of the determinant will be unchanged, unless the determinant be of odd order and a principal diagonal be one of the diagonals whose elements are changed, in which case the value of the determinant will be changed in sign, and sign only.

The theorem is established directly from the following lemma :—

Lemma.—Let A and B be two sets of numbers, each consisting of the integers 1, 2, 3, 4, . . ., n. Let n number pairs (i, j) be formed, i being a number of set A and j being a number of set B, so that each number in A, and likewise each number in B, occurs once and only once in a pair. In all cases there will be an even number of pairs the sum of whose integers, $i+j$, is odd.

Proof of Lemma.—We shall call a pair an even pair if the sum of the integers is even, and an odd pair if the sum of the integers is odd. Now $i+j$ can be even only if both i and j are even, or both odd. Let A_1 and B_1 be the sets remaining after removing from A and B, respectively, the numbers used in forming even pairs, for any possible pairing according to the lemma. Let k be the number of even numbers in A_1. Then there will be k even numbers in B_1, since A and B are

* Communicated by the Author.

identical, and the same number of evens are removed from each. Also since the numbers of A_1 and B_1 form odd pairs, the even numbers of A_1 must be paired with the odd numbers of B_1, so that there must be k odd numbers in B_1. Hence B_1, and likewise A_1, must contain $2k$ numbers. Consequently the number of odd pairs is always even.

Corollary.—For any set of n pairs formed according to the conditions of the lemma there will be an even number of even pairs if n be even, and an odd number of even pairs if n be odd.

This is a direct result of the lemma, in which it was shown that the number of odd pairs is always an even number.

Proof of Theorem.—The terms in the expansion of a determinant of order n each consist of n factors of the form, a, the row and column indices forming a number pair for each factor. By a familiar law of determinants these pairs occur in any term of the expansion exactly as the sets of number pairs in the lemma above. Now in a set of alternate diagonals which does not include a principal diagonal all of the elements are such that $i+j$ is odd. These index pairs correspond to odd pairs in the lemma. Consequently there must be an even number of such pairs, *i. e.*, there must be an even number of factors from this set of diagonal elements in any term of the expansion of the determinant. Hence changing the signs of all these elements will not affect any term in the expansion, proving the first part of the theorem.

In a set of alternate diagonals which does include a principal diagonal, every element is such that $i+j$ is even, corresponding to an even pair in the lemma. By the corollary there will be an even number or an odd number of such pairs, according as n is even or n is odd, *i. e.*, there will be in each term of the expansion of the determinant an even number or an odd number of factors from this set of elements, according as n is even or odd. Then, if the sign of each element in such a set of alternate diagonals be changed, the terms in the expansion of the determinant will be unchanged or else all changed in sign, according as n is even or n odd. Hence the theorem.

Though it furnishes nothing new, it might be noted that the theorem with reference to change of sign of elements in alternate diagonals is also true when stated for change of sign of elements in alternate rows (or columns), principal diagonal being replaced by middle row (or column).

This theorem will be found to have special application in

continuants. Its application to determinants of the third and fourth orders is shown below :—

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = \begin{vmatrix} a_{11} & -a_{12} & a_{13} \\ -a_{21} & a_{22} & -a_{23} \\ a_{31} & -a_{32} & a_{33} \end{vmatrix} = -\begin{vmatrix} -a_{11} & a_{12} & -a_{13} \\ a_{21} & -a_{22} & a_{23} \\ -a_{31} & a_{32} & -a_{33} \end{vmatrix}$$

$$\begin{vmatrix} a_{11} & a_{12} & a_{13} & a_{14} \\ a_{21} & a_{22} & a_{23} & a_{24} \\ a_{31} & a_{32} & a_{33} & a_{34} \\ a_{41} & a_{42} & a_{43} & a_{44} \end{vmatrix} = \begin{vmatrix} a_{11} & -a_{12} & a_{13} & -a_{14} \\ -a_{21} & a_{22} & -a_{23} & a_{24} \\ a_{31} & -a_{32} & a_{33} & -a_{34} \\ -a_{41} & a_{42} & -a_{43} & a_{44} \end{vmatrix} = \begin{vmatrix} -a_{11} & a_{12} & -a_{13} & a_{14} \\ a_{21} & -a_{22} & a_{23} & -a_{24} \\ -a_{31} & a_{32} & -a_{33} & a_{34} \\ a_{41} & -a_{42} & a_{43} & -a_{44} \end{vmatrix}$$

University of South Carolina,
Columbia, S. C.,
October, 1929.

LVII. *Graphic Statistics : Permille Paper.*

By A. F. Dufton, *M.A., D.I.C.**

1. IT is convenient to represent a frequency-distribution by means of a curve or diagram, which conveys the general run of the observations to the eye better than a column of figures, and for this purpose Galton's ogive, the frequency-polygon and the histogram are commonly used.

Galton's method has the advantage that the meaning of the various percentiles is simple and readily understood. The ogive curve, however, does not bring out any asymmetry in the distribution so clearly as does the frequency-polygon. None of the methods shows at a glance whether the distribution is normal.

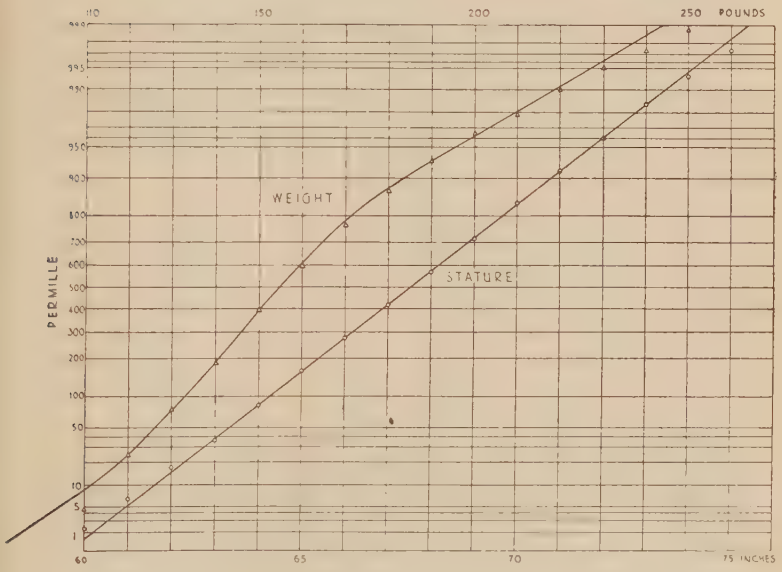
In the method of representation now proposed, the figures of the original table are added up step by step, so as to give the total frequency not exceeding the upper limit of each class interval, and ordinates are then erected to a horizontal base to represent, to a special scale, these integrated frequencies as parts permille ; a smooth curve may be drawn through the tops of the ordinates. The special frequency scale is the scale of deviates of the

* Communicated by the Author.

normal curve for each permille of frequency *. When drawn to this scale a normal frequency-distribution is of course represented by a straight line.

2. In illustration of this method it is of interest to consider the curves obtained for two examples of vital statistics—the frequency-distribution of statures for adult males born in Great Britain and Ireland and the frequency-distribution of weights † (fig. 1). It is clear

Fig. 1.



that the frequency-distribution of stature is sensibly normal while that of weight is asymmetrical.

The weight-curve is not analytically simple. The smooth curve drawn, however, is of interest as it represents the normal distribution for a population of which two-thirds have an average weight of 152 pounds, with a standard deviation of 14 pounds, and one-third an average weight of 166 pounds, with a standard deviation of 28 pounds.

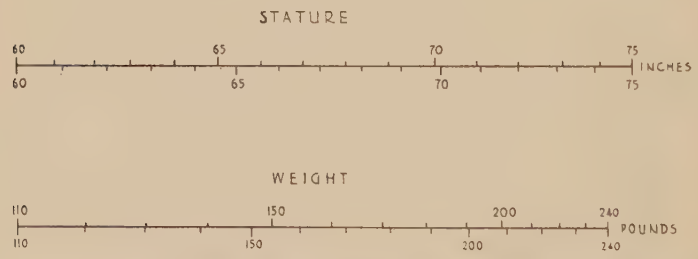
* 'Tables for Statisticians and Biometricians,' p. 1.

† Yule, 'Theory of Statistics,' pp. 88 & 95.

3. By an anamorphosis the curve can be transformed into a straight line, a scale of measurement being determined which makes the frequency-distribution normal: this may be of advantage when the functional scale so obtained is simple.

In a paper on "The Geometric Mean in Vital and Social Statistics" * Galton states that the ordinary law of Frequency of Error, based on the arithmetic mean, corresponds sufficiently well with the observed facts of vital and social phenomena to be very serviceable to statisticians, but is far from satisfying their wants and may lead to absurdity when applied to wide deviations. Thus the law is very correct in respect to ordinary measurements of stature, although it asserts that the existence of giants, whose height is more than double the mean height of their race, implies the possibility of dwarfs

Fig. 2.



whose stature is less than nothing at all. Galton concludes that vital and sociological phenomena are, as a general rule, subject to the condition of the geometric mean and suggests that they are properly measured in logarithmic units.

In fig. 2 the functional scales for stature and weight are shown which make the frequency-distributions normal. Each is drawn above a logarithmic scale and it is clear that these two examples do not support Galton's contention.

4. It would appear desirable to have a name for the coordinate paper upon which the frequency curves are plotted: the name *Permille* is suggested.

Greenbank, Garston,
Hertfordshire.

* Proc. Roy. Soc. xxix. p. 365 (1879).

LVIII. *The Electrical Conductivities of Dilute Sodium Amalgams at various Temperatures.* *By* W. J. Davies, *M.Sc., and Professor* E. J. Evans, *D.Sc., Physics Department, University College of Swansea* *.

THE present research is a continuation of the systematic investigations carried out by several observers† in the Physical Laboratories of the University College of Swansea on the conductivities of dilute amalgams at various temperatures.

As the amalgams hitherto examined were those of metals belonging to Groups II., III., and IV. of the periodic table, it was decided to measure as accurately as possible the electrical conductivities of amalgams of sodium, a metal belonging to Group I. of the periodic table. Previous work carried out at Swansea and elsewhere has shown that the solution of metals in mercury causes an increase in conductivity, but this does not appear to be the case for alkali amalgams. These amalgams differ in other respects from the amalgams of other metals. Their formation is accompanied by the evolution of a great amount of heat, and their viscosity ‡ is greater than that of the amalgams of other metals.

Measurements of the electrical conductivities of sodium amalgams have been carried out by Batelli §, Grimaldi ‖, Vanstone ¶, Müller **, Bornemann and Rauschenplatt ††, Rogers ‡‡, Feninger §§, Lewis and Hine ‖‖, and Boohariwalla, Paranjpe and Prasad ¶¶.

* Communicated by Prof. E. J. Evans, D.Sc.

† E. J. Williams, Phil. Mag. p. 589 (September 1925); T. I. Edwards, Phil. Mag. p. 1 (July 1926); A. L. Johns and E. J. Evans, Phil. Mag. p. 271 (February 1928); T. C. Williams and E. J. Evans, Phil. Mag. p. 1231 (December 1928).

‡ Feninger, 'Die Electrische Leitfähigkeit und innere Reibung Verdunter Amalgame,' Freiburg (1914).

§ Atti Accad. Lincei, [4] iii. p. 19 (1887).

‖ Atti Accad. Lincei, [4] iii. p. 32 (1887).

¶ Journ. Chem. Soc. cv. p. 2617 (November 1914).

** 'Metallurgie,' vii. p. 767 (1910).

†† 'Metallurgie,' ix. p. 510 (1910).

‡‡ Phys. Rev. [2] viii. p. 259 (1916).

§§ *Loc. cit.*

‖‖ Nat. Accad. Sci. Proc. ii. p. 634 (November 1916); Journ. Amer. Chem. Soc. [39] i. p. 882 (May 1917).

¶¶ Indian Journ. Phys. iv. pt. ii. p. 14 (April 1929).

Vanstone was chiefly concerned with the conductivities of solid amalgams and concentrated liquid amalgams; but Müller and Bornemann and Rauschenplatt determined the electrical conductivities of a few dilute sodium amalgams of different concentrations at temperatures varying from 50° C. to 350° C. Feninger, in addition to measuring the conductivities of dilute amalgams containing 0·201, 0·761, 1·192, 2·175, and 2·690 gram atoms per cent. of sodium, determined the viscosities of the amalgams at room temperature. The two most recent investigations of the electrical conductivities of sodium amalgams are due to Lewis and Hine *, and Boohariwalla, Paranjpe and Prasad †.

The former investigators determined at a temperature of 20° C. the relative conductivities (*i.e.*, the conductivities with respect to mercury at the same temperature) of eleven sodium amalgams of concentrations ranging from 0·09 to 4·9 gram atoms per cent. of sodium, and the latter measured the electrical conductivities at 30° C. of eighteen sodium amalgams of concentrations ranging from 0·159 to 2·75 gram atoms per cent.

As the results of the above investigations are not in agreement, and comparatively few experiments had been carried out at temperatures above 80° C., it was hoped that the present investigation, which deals with the conductivities of dilute sodium amalgams of concentrations varying from 0·307 atom per cent. to 5·270 atoms per cent. at temperatures ranging from 0° C. to about 300° C., would throw further light on the problem.

The accurate determination of the electrical conductivities is difficult, especially at high temperatures, as sodium amalgams readily oxidize and react chemically with the glass or quartz of the containing vessel. From the experimental results are calculated certain quantities which are of importance in a theory of the conductivity of amalgams put forward by Skaupy ‡. If L and η represent the conductivity and viscosity respectively of pure mercury, and ΔL, $\Delta\eta$ the change in conductivity and viscosity due to a concentration C of the metal expressed in gram atoms dissolved in 100 gram atoms of mercury,

* *Loc. cit.* † *Loc. cit.*

‡ *Zeit. für Phys. Chem.* lxviii. p. 560 (1907); *Verh. Deut. Phys. Ges.* xvi. p. 156 (1914); *ibid.* xviii. p. 252 (1916); *Phys. Zeit.* xxi. p. 597 (1920).

then, according to Skaupy, the value of $\frac{I}{C}\frac{\Delta L}{L}+\frac{I}{C}\frac{\Delta\eta}{\eta}$ at infinite dilution is of the same order of magnitude for all metals dissolved in mercury.

If l is written for $\frac{1}{C}\frac{\Delta L}{L}$ and r for $\frac{1}{C}\frac{\Delta\eta}{\eta}$,

then $$H=\frac{1}{C}\frac{\Delta L}{L}+\frac{1}{C}\frac{\Delta\eta}{\eta}=l+r,$$

and

$$H_\infty=l_\infty+r_\infty.$$

Skaupy* also considered the variation of H with concentration, and came to the conclusion that $\frac{H_\infty-H}{C}$ should be constant. If the variation of viscosity with concentration can be neglected, it follows that l_∞ should be of the same order of magnitude for all metals dissolved in mercury, and that $\frac{l_\infty-l}{C}$ should be constant.

The experiments carried out in this laboratory seem to lend support to these conclusions in the case of amalgams of metals belonging to Groups II., III., and IV. of the Periodic Table. For example, Williams and Evans† have shown that l_∞ has practically the same value for amalgams of copper, silver, and gold at the same temperature, and also that the relation between $l_\infty-l$ and the concentration C is a linear one. The possible application of Skaupy's relations to the experimental results obtained for sodium amalgams will be discussed later.

Experimental Arrangement.

General Principle of Method.

The general principle of the method of measurement is the same as that employed by other investigators working in this laboratory, but various modifications were made in the apparatus owing to the special properties of alkali amalgams.

The conductivity of mercury or an amalgam of given concentration was determined by measuring the electrical

* *Loc. cit.* † *Loc. cit.*

resistance of a fine column of the liquid conductor by means of a Callendar-Griffiths bridge in conjunction with a moving coil galvanometer of high sensitivity. The resistances of the bridge were all calibrated in terms of the largest resistance, and thus the relative values of the bridge resistances were accurately known. These relative values are sufficient for an accurate determination of the temperature coefficient of resistivity of pure mercury or of an amalgam, and the absolute value of the resistivity of an amalgam at any temperature can be deduced, if the resistivity of mercury at 0° C. is taken as 94074×10^{-9} ohm per cm.[3]

If ${}_aR_t$ be the resistance of the amalgam column of length l and cross-section A at temperature t° C., ${}_a\rho_t$ its resistivity, and ${}_m\mathrm{R}_t$, ${}_m\rho_t$ the corresponding quantities for mercury, it then follows that :—

$$ {}_a\rho_t = \frac{{}_a\mathrm{R}_t}{{}_m\mathrm{R}_t} \cdot {}_m\rho_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1) $$

From equation (1) it is easily seem that the resistivity and conductivity of an amalgam at a temperature t° C. can be calculated from the resistivity of mercury at the same temperature, and the corresponding values of the resistances of the amalgam and mercury columns. The resistivity of pure mercury at any temperature can be calculated from the equation :—

$$ \rho_t = 94074 \times 10^{-9}[1 + {\cdot}0_3 8877t + {\cdot}0_6 977t^2 + {\cdot}0_9 19t^3], $$

which represents the results of experiments carried out by Williams * and Edwards † on the resistivity of mercury at temperatures up to 300° C. This equation also represents, within experimental error, the results for pure mercury obtained with the modified apparatus employed in the present research.

An amalgam of a given concentration was heated to a definite temperature by immersing the capillary tube in an iron bath containing a suitable liquid, which could be raised to the boiling point by a burner consisting of a long row of small flames protected from draughts. The liquids employed were methylated spirits, water, aniline, diethylaniline, engenol, and diphenylamine, and consequently measurements could be made at temperatures in the neighbourhood of 20° C. (room temperature), 78° C.,

* *Loc. cit.* † *Loc. cit.*

100° C., 185° C., 225° C., 255° C., and 300° C. Since measurements were also carried out at the temperature of melting ice, it was possible to study the resistivity of an amalgam over a temperature range of 300° C., and measurements at a particular temperature were made under practically constant conditions, as the temperature of the boiling liquids only changed very gradually. The temperatures of the amalgam column were determined by a platinum resistance thermometer, which had been previously calibrated, and also by a suitable mercury thermometer. A set of mercury thermometers, which had been calibrated at the National Physical Laboratory, were used in these measurements. The degree of accuracy attained in the measurement of the bath temperature, when the liquid was boiling steadily, is indicated by the fact that the platinum and mercury thermometers agreed to within 0·1° C., even at 300° C. By taking a large number of observations, the resistance of the capillary column could be determined wth an accuracy of about 0·00005 ohm, and since the resistance of the column at 0° C. was almost 0·29 ohm, it can be calculated from the observations that a change of resistance of 0·00005 ohm. corresponds to a change of temperature of 0·19° C. at 100° C., and to about 0·1° C. at 300° C. It is, therefore, seen that the measurement of temperature is of the required order of accuracy.

Preparation of the Amalgam, and the Measurement of its Resistivity.

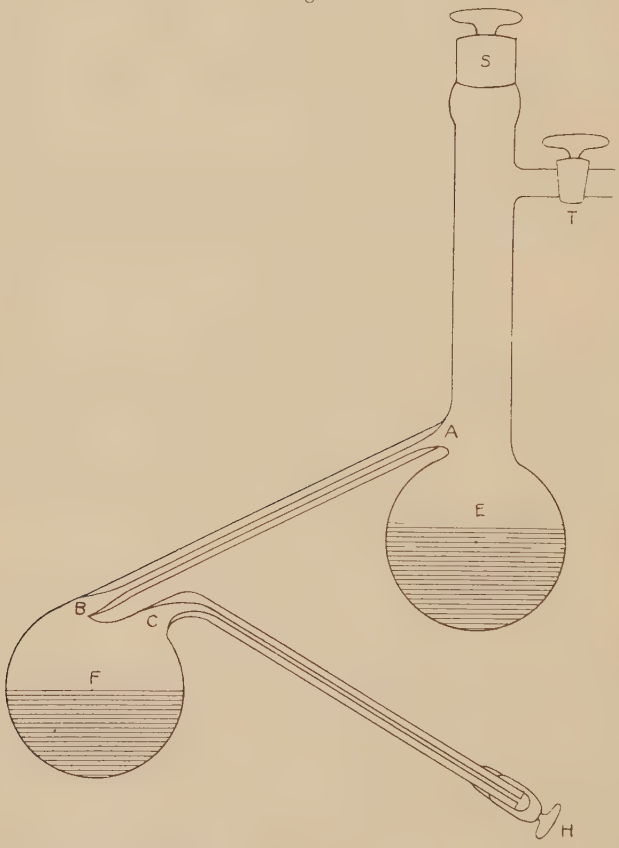
The special properties of the amalgam, such as its affinity for oxygen especially in presence of moisture and its chemical action on glass, necessitated certain modifications in methods previously employed * for measuring the resistivities of other amalgams.

In the present experiments a quantity of concentrated liquid sodium amalgam was prepared by adding pure sodium contained in a sealed glass tube to a suitable quantity of pure redistilled mercury. The mercury was introduced into a conical flask, which was closed with a tightly fitting stopper, through which passed a bent glass tube connected to a glass tap by means of a short length of pressure tubing. The end of the bent tube outside the

* T. I. Edwards, *loc. cit.*

flask had been drawn out to a fairly narrow bore. The flask was evacuated and then filled with pure dry nitrogen at atmospheric pressure ; the stopper was then removed, and the sealed glass tube containing the sodium was broken and dropped into the mercury. The stopper was then quickly replaced, the flask evacuated, and the mercury

Fig. 1.



warmed until a uniform solution of amalgam was obtained. On cooling, nitrogen was again introduced into the flask, which contained a large quantity of concentrated amalgam, suitable for the preparation of dilute amalgams of various concentrations. This amalgam was, however, covered with oxide films, which were removed by the filtering apparatus sketched in fig. 1.

A large glass bulb E, provided with a tap T and a ground-glass stopper S, was connected with a similar bulb F by means of a coarse capillary tube AB. The bulb F was also provided with a fine capillary tube CH, the end of which was closed by a tightly fitting cap H. The apparatus was evacuated and filled with nitrogen through the tap T. The pressure tubing and tap were removed from the conical flask, and also the stopper S from the filtering apparatus, so that the amalgam could be poured into the bulb E, which was immediately sealed up by replacing the stopper. The apparatus was evacuated, to remove any air which had possibly diffused into the nitrogen during the operation of pouring, and was again filled with pure dry nitrogen. The amalgam contained in the bulb E was bright and clean, as most of the oxide films were removed when it passed through the constricted portion of the bent glass tube attached to the conical flask. The films remaining were almost completely removed by tilting the filtering apparatus so that the amalgam passed through the capillary tube AB into the bulb F. The concentrated liquid amalgam was kept in this bulb in an atmosphere of pure dry nitrogen until required for the preparation of a dilute amalgam of given concentration in the four-electrode resistance tube.

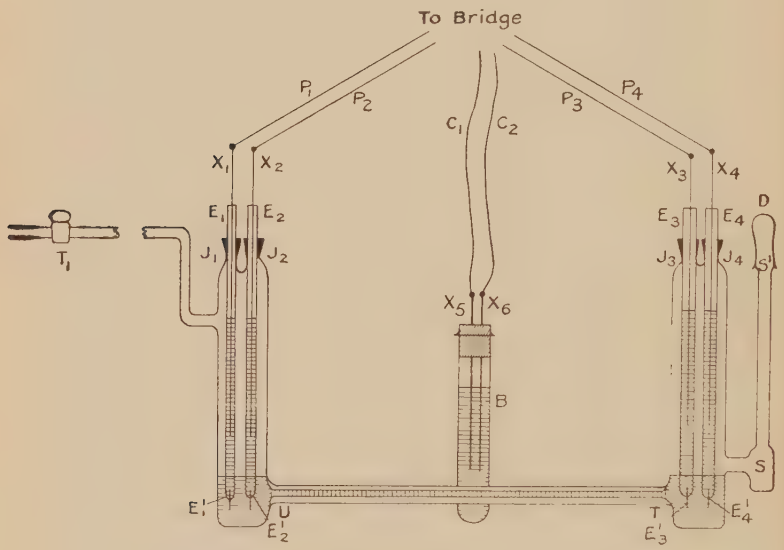
The four-electrode pyrex-glass tube which was employed in measuring the resistances of the amalgams is shown in fig. 2.

The four electrodes consisted of similar glass tubes, $E_1E_1^1$, $E_2E_2^1$, $E_3E_3^1$, and $E_4E_4^1$, through the lower ends of which platinum wires were sealed. The tubes were half-filled with mercury into which dipped stout copper wires, X_1, X_2, X_3, and X_4, which could be connected to the Callendar-Griffiths bridge through a specially constructed mercury key by means of flexible leads, P_1, P_2, P_3, and P_4. The compensating leads, C_1 and C_2, were soldered to copper wires, X_5 and X_6, which dipped into mercury contained in the test-tube B. This test-tube was placed in the bath near the centre of the capillary, UT, and the compensating leads were also permanently connected to the bridge through the mercury key.

As the amalgam oxidizes readily, it was necessary to work in an atmosphere of an inert gas, and with this end in view the apparatus was in the first place made gas-tight. This was accomplished by painting the ground electrode

joints, J_1, J_2, J_3, and J_4, with cellulose cement, and by sealing the dome D on the ground end of the vertical tube SS′ with white wax. The apparatus could be connected to a pump or a cylinder containing nitrogen through the tap T, which was lubricated with ordinary tap grease. The tap was placed at a sufficient distance from the bath for the grease to be not affected by the bath, and the amalgam was not contaminated by grease films. A dilute amalgam of the required concentration was now prepared as follows :—

Fig. 2.



A known-weight of pure re-distilled mercury was introduced into the resistance tube through the upright limb SS^1, and the dome D replaced. The tube was evacuated, and filled with nitrogen at atmospheric pressure. The nitrogen was freed from oxygen by passing over red-hot copper, and was also carefully dried. The concentration of the amalgam contained in the bulb F of the filtering apparatus was determined by running out a known-weight through the fine capillary CH into a conical flask, and adding a known volume of standard HCL solution until there was an excess of acid present, when all the sodium had come out of solution in mercury. The excess of acid

was then titrated with a standard solution of sodium carbonate, and from the results the weight of sodium contained in 100 grams of mercury could be calculated in the usual manner. The concentration of the amalgam having thus been determined, it was possible, after experience, to run into the resistance tube approximately the correct amount of concentrated amalgam to produce on admixture with pure mercury a dilute amalgam of the desired concentration. For this purpose the dome D was removed, and the concentrated amalgam run into the tube from the filtering apparatus. This operation was carried out quickly, and both the resistance tube and, filtering apparatus were immediately sealed up again. The resistance tube was then evacuated to a pressure of 1/100 mm. of mercury, to get rid of air which may have diffused into the nitrogen on removing the dome, and, finally, a sufficient quantity of pure dry nitrogen was allowed to enter the tube to produce a pressure of one atmosphere at 300° C. After the resistivities of the dilute amalgam had been measured at various temperatures from 0° C. to 300° C., the amalgam was run out into a conical flask, and its concentration again determined by the method previously described.

The method adopted for measuring the resistance of the amalgam column can be readily understood from fig. 2.

The resistances of the copper wires $X_1 \ldots X_6$ were equal, and the flexible copper leads $P_1 \ldots P_4$, C_1, and C_2, which also had equal resistances, were placed side by side close together, so that changes of temperature would affect their resistances equally. The following measurements were carried out with the Callendar-Griffiths bridge :—

(1) P_1 and P_4 were connected to the bridge and the resistance measured. Let R_1 be the resistance.
(2) P_2 and P_3 were connected to the bridge. Let R_2 be the resistance.
(3) P_1 and P_2 were connected to the bridge. Let R_3 be the resistance.
(4) P_3 and P_4 were connected to the bridge. Let R_4 be the resistance.

If R be the resistance of the amalgam column UT between the two inner electrodes, it can be shown that

$$R = \tfrac{1}{2}[(R_1+R_2)-(R_3+R_4)].$$

In this way the resistances of the various amalgam columns were determined and the electrode resistances eliminated.

Experimental Difficulties.

The pyrex-glass resistance tube employed in the present investigation, after exposure to high temperatures for several hours, showed evidence of having been slightly attacked by the sodium amalgam. It was also noticed that the formation of bubbles in the capillary, at temperatures above 100° C., was far more prevalent with sodium amalgams than with the other amalgams examined in this laboratory. It is therefore probable that the formation of bubbles is partly due to the chemical action of the amalgam on the glass. These bubbles were removed by placing the tube containing the amalgam in a metal air-bath, which could be tilted in a vertical plane about a fulcrum, and also heated to a temperature above that at which the resistance of the amalgam was measured. By gradually tilting the tube the amalgam was slowly passed through the capillary, and the operation was repeated until the capillary, when examined by a lens, showed no trace of bubbles. Even when bubbles had been removed in this way they frequently reappeared if the tube was kept at a temperature between 250° C. and 300° C. for an interval of one hour. After the resistance of the amalgam had been determined at a temperature above 100° C., it was removed from the liquid heating bath and the capillary carefully examined for bubbles. If there were no bubbles present, and if the resistance determined at room temperature agreed with the value previously obtained, the high temperature measurement was considered satisfactory.

The analysis of the amalgam, after a set of observations, always indicated a slight loss of concentration as compared with that expected on mixing the amalgam from the filtering apparatus with the pure mercury in the tube. The concentrations given in Tables I. to VIII. are the ones obtained by analysing the amalgams, run out of the tube at the end of each set of experiments with an amalgam of given concentration. It is considered that the concentrations corresponding to the resistivities and conductivities given in these tables are correct to within $\frac{1}{2}$ per cent. for the more concentrated amalgams, and to within 2 per cent.

for the very dilute amalgams. An inspection of the experimental results, however, shows that the concentration measurements are of sufficient accuracy as compared with the resistivity measurements.

The slight loss in the concentration of the sodium amalgam was also accompanied by a small increase in the diameter of the tube. The tube was cleaned and calibrated with pure mercury at 0° C. and 100° C. after each set of experiments with an amalgam of definite concentration. It was found, after the first set of experiments, that the resistance of the mercury column had diminished by about 1 in 3000 as compared with its original value. A similar decrease was observed after each set of amalgam determinations, but its magnitude diminished progressively. This effect of the amalgam on the diameter of the resistance tube was taken into account in calculating the resistivities and conductivities of the various amalgams.

Although this loss in the concentration of the amalgam was in all probability mainly due to the chemical action of the amalgam on the glass, a small part may possibly be due to oxidation as a consequence of (i.) a small leak of air into the apparatus on removal of the dome when introducing the concentrated amalgam into the tube, and of (ii.) the presence of air films adhering firmly to the glass surface.

At high temperatures, the effect of thermoelectric currents was very noticeable, but it was overcome by first closing the galvanometer circuit and adjusting the bridge resistance until there was no change in the deflexion on completing the battery circuit. Under these conditions, in virtue of the properties of conjugate conductors, the bridge resistance is equal to the resistance being measured. The very small inductance of the amalgam column caused no trouble.

It is estimated that the average error in the measurements of the resistivities and conductivities is not greater than about 1 in 7000, and that the possible error in the calculated values of $\frac{\Delta L}{L}$ and $\frac{I}{C}\frac{\Delta L}{L}$ is about 8 per cent. for the lowest concentrations and about 2 per cent. for the high concentrations. The average temperature coefficient of resistance is estimated to be correct within 0·9 per cent. over the temperature range 0° C. to 20° C., and within about 0·06 per cent. over the range 0° C. to 300° C.

Table I.

Results for Eleven Sodium Amalgams of different Concentrations at a Constant Temperature of 0° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $_{m}R_{t}$.	Resistance in ohms. $_{a}R_{t}$.	Relative resistivity $\frac{{}_{a}R_{t}}{{}_{m}R_{t}}$.	Average temperature coefficient of resistivity of Hg from 0° to t° C., = $_{m}a_{t}$.	Average temperature coefficient of resistivity of Amalgam from 0° to t° C., = $_{a}a_{t}$.	Resistivity of Hg at t° C., $_{m}\rho_{t}\times10^{8}$.	Resistivity of Sodium Amalgam at 0° C., $_{a}\rho_{t}\times10^{8}$.	Conductivity of Hg at 0° C., $_{m}L_{t}$.	Conductivity of Sodium Amalgam at 0° C., $_{a}L_{t}$.	$\frac{\Delta L}{L}\times10^{2}$.	$\frac{1}{C}\cdot\frac{\Delta L}{L}\times10^{2}$.
1	$\cdot035_{2}$	$\cdot30_{7}$	$\cdot2891_{8}$	$\cdot2898_{5}$	$1\cdot0023_{2}$	——	——	9407	9429	10630	10605	$-\cdot23_{5}$	$-\cdot77$
2	$\cdot052_{1}$	$\cdot45_{4}$	$\cdot2891_{5}$	$\cdot2901_{0}$	$1\cdot0032_{9}$	——	——	9407	9438	10630	10595	$-\cdot32_{9}$	$-\cdot72$
3	$\cdot076_{2}$	$\cdot66_{4}$	$\cdot2891_{7}$	$\cdot2904_{3}$	$1\cdot0043_{6}$	——	——	9407	9448	10630	10584	$-\cdot43_{3}$	$-\cdot65$
4	$\cdot106$	$\cdot92_{2}$	$\cdot2716_{8}$	$\cdot2731_{2}$	$1\cdot0053_{0}$	——	——	9407	9457	10630	10574	$-\cdot52_{7}$	$-\cdot57$
5	$\cdot136$	$1\cdot18_{4}$	$\cdot2715_{5}$	$\cdot2734_{0}$	$1\cdot0068_{1}$	——	——	9407	9471	10630	10558	$-\cdot67_{7}$	$-\cdot57$
6	$\cdot212$	$1\cdot84_{9}$	$\cdot2714_{3}$	$\cdot2735_{4}$	$1\cdot0077_{7}$	——	——	9407	9480	10630	10548	$-\cdot77_{1}$	$-\cdot42$
7	$\cdot262$	2·29	$\cdot2713_{8}$	$\cdot2735_{0}$	$1\cdot0078_{1}$	——	——	9407	9481	10630	10548	$-\cdot77_{1}$	$-\cdot33$
8	$\cdot297$	2·59	$\cdot2713_{8}$	$\cdot2734_{3}$	$1\cdot0075_{5}$	——	——	9407	9478	10630	10551	$-\cdot74_{3}$	$-\cdot29$
9	$\cdot354$	3·08	$\cdot2893_{5}$	$\cdot2917_{1}$	$1\cdot0081_{6}$	——	——	9407	9484	10630	10544	$-\cdot80_{9}$	$-\cdot26$
10	$\cdot458$	3·99	$\cdot2893_{0}$	$\cdot2911_{0}$	$1\cdot0062_{2}$	——	——	9407	9466	10630	10564	$-\cdot62_{1}$	$-\cdot15_{5}$
11	$\cdot604$	5·27	$\cdot2891_{5}$	$\cdot2881_{6}$	$\cdot9965_{8}$	——	——	9407	9375	10630	10666	$+\cdot34_{0}$	$+\cdot06$

Table II.

Results for Eleven Dilute Sodium Amalgams at a Constant Temperature of 20° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $m R_{20°}$.	Resistance in ohms. $a R_{20°}$.	Relative resistivity $\frac{a R_{20°}}{m R_{20°}}$.	Average temperature coefficient of resistivity of Mercury from 0° to 20° C., $= m\alpha_t$.	Average temperature coefficient of resistivity of Amalgam from 0° to 20° C., $= a\alpha_t$.	Resistivity of Mercury at 20° C., $m\rho_{20°} \times 10^3$.	Resistivity of Amalgam at 20° C., $a\rho_{20°} \times 10^3$.	Conductivity of Mercury at 20° C., $m L_{20°}$.	Conductivity of Amalgam at 20° C., $a L_{20°}$.	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{C} \cdot \frac{\Delta L}{L} \times 10^2$.
1	$\cdot 035_2$	$\cdot 30_7$	$\cdot 2944_1$	$\cdot 2951_2$	$1 \cdot 0024_1$	$\cdot 0_3907$	$\cdot 0_3912$	9578	9601	10440	10415	$-\cdot 24$	$-\cdot 78$
2	$\cdot 052_1$	$\cdot 45_4$	$\cdot 2943_8$	$\cdot 2954_8$	$1 \cdot 0037_3$	0_3907	$\cdot 0_3932$	9578	9614	10440	10402	$-\cdot 36_4$	$-\cdot 80$
3	$\cdot 076_2$	$\cdot 66_4$	$\cdot 2944_0$	$\cdot 2957_6$	$1 \cdot 0046_2$	$\cdot 0_3907$	$\cdot 0_3921$	9578	9622	10440	10392	$-\cdot 45_9$	$-\cdot 69$
4	$\cdot 106$	$\cdot 92_2$	$\cdot 2765_9$	$\cdot 2781_7$	$1 \cdot 0057_1$	$\cdot 0_3907$	$\cdot 0_3930$	9578	9633	10440	10381	$-\cdot 56_5$	$-\cdot 61$
5	$\cdot 136$	$1 \cdot 18_4$	$\cdot 2764_6$	$\cdot 2784_7$	$1 \cdot 0072_7$	$\cdot 0_3907$	$\cdot 0_3934$	9578	9648	10440	10365	$-\cdot 71_9$	$-\cdot 61$
6	$\cdot 212$	$1 \cdot 84_9$	$\cdot 2763_4$	$\cdot 2789_2$	$1 \cdot 0093_4$	$\cdot 0_3907$	$\cdot 0_3986$	9578	9667	10440	10344	$-\cdot 92_0$	$-\cdot 50$
7	$\cdot 262$	$2 \cdot 29$	$\cdot 2762_9$	$\cdot 2787_7$	$1 \cdot 0089_8$	$\cdot 0_3907$	$\cdot 0_3965$	9578	9664	10440	10348	$-\cdot 88_1$	$-\cdot 38$
8	$\cdot 297$	$2 \cdot 59$	$\cdot 2762_9$	$\cdot 2786_3$	$1 \cdot 0084_7$	$\cdot 0_3907$	$\cdot 0_3955$	9578	9659	10440	10353	$-\cdot 83_3$	$-\cdot 32$
9	$\cdot 354$	$3 \cdot 08$	$\cdot 2945_8$	$\cdot 2973_5$	$1 \cdot 0094_0$	$\cdot 0_3907$	$\cdot 0_3970$	9578	9668	10440	10343	$-\cdot 92_9$	$-\cdot 30$
10	$\cdot 458$	$3 \cdot 99$	$\cdot 2945_3$	$\cdot 2967_2$	$1 \cdot 0067_4$	$\cdot 0_3907$	$\cdot 0_3972$	9578	9650	10440	10363	$-\cdot 73_8$	$-\cdot 18_5$
11	$\cdot 604$	$5 \cdot 27$	$\cdot 2943_6$	$\cdot 2957_2$	$1 \cdot 0046_2$	$\cdot 0_3907$	——	9578	9622	10440	10393	$-\cdot 45_0$	$-\cdot 08_5$

Table III.

Results for Eleven Dilute Liquid Sodium Amalgams at a Constant Temperature of 78·4° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $_m R_t$.	Resistance in ohms. $_a R_t$.	Relative resistivity or ratio $\frac{_a R_t}{_m R_t}$.	Average temperature coefficient of increase of resistivity of Mercury from 0° to 78·4° C., = $_m\alpha_t$.	Average temperature coefficient of resistivity of Amalgam over 0° to 78·4° C., = $_a\alpha_t$.	Resistivity of Mercury at 78·4° C., $_m\rho_t \times 10^3$.	Resistivity of Amalgam at 78·4° C., $_a\rho_t \times 10^3$.	Conductivity of Mercury at 78·4° C., $_m L_t$.	Conductivity of Amalgam at 78·4° C., $_a L_t$.	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{C} \cdot \frac{\Delta L}{L} \times 10^2$.
1	·035$_2$	0·30$_7$	·3110$_0$	·3121$_0$	1·0035$_0$	·$_0$3965	·$_0$2982	10119	10155	9882	9848	− ·34$_4$	−1·12
2	·052$_1$	0·45$_4$	·3109$_6$	·3124$_0$	1·0046$_3$	·$_0$3965	·$_0$3984	10119	10166	9882	9837	− ·45$_5$	−1·00
3	·076$_2$	0·66$_4$	·3109$_8$	·3123$_9$	1·0061$_4$	·$_0$3965	·$_0$3990	10119	10181	9882	9822	− ·61	− ·92
4	·106	0·92$_2$	·2921$_8$	·2944$_2$	1·0076$_6$	·$_0$3965	·$_0$3998	10119	10197	9882	9807	− ·75$_9$	− ·82
5	·136	1·18$_4$	·2920$_3$	·2947$_2$	1·0092$_1$	·$_0$3965	·$_0$3998	10119	10212	9882	9792	− ·91$_1$	− ·77
6	·212	1·84$_9$	·2919$_1$	·2952$_7$	1·0115$_1$	·$_0$3965	·$_0$2 1017	10119	10236	9882	9770	−1·13$_3$	− ·61
7	·262	2·29	·2918$_6$	·2951$_8$	1·0113$_8$	·$_0$3965	·$_0$2 1013	10119	10234	9882	9771	−1·12$_3$	− ·49
8	·297	2·59	·2918$_5$	·2951$_9$	1·0114$_4$	·$_0$3965	·$_0$2 1016	10119	10235	9882	9771	−1·12$_3$	− ·43
9	·354	3·08	·3111$_8$	·3150$_9$	1·0122$_7$	·$_0$3965	·$_0$2 1021	10119	10243	9882	9763	−1·20$_4$	− ·39
10	·458	3·99	·3111$_2$	·3142$_7$	1·0101$_2$	·$_0$3965	·$_0$2 1019	10119	10222	9882	9783	−1·00$_2$	− ·25
11	·604	5·27	·3109$_6$	·3129$_8$	1·0064$_9$	·$_0$3965	——	10119	10185	9882	9818	− ·65$_2$	− ·12$_4$

Table IV.

Results for Eleven Dilute Liquid Sodium Amalgams at a Constant Temperature $t = 100°$ C

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $_m R_t$.	Resistance in ohms. $_a R_t$.	Relative resistivity or ratio $\frac{_a R_t}{_m R_t} = {}_m\alpha_t$.	Average temperature coefficient of resistivity of Hg from 0° to 100° C., $= {}_m\alpha_t$.	Average temperature coefficient of resistivity of Amalgam from 0° to 100° C., $= {}_a\alpha_t$.	Resistivity of Mercury at 100° C., $_m\rho_t \times 10^8$.	Resistivity of Amalgam at 100° C., $_a\rho_t \times 10^8$.	Conductivity of Mercury at 100° C., $_m L_t$.	Conductivity of Amalgam at 100° C., $_a L_t$.	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{C} \cdot \frac{\Delta L}{L} \times 10^2$.
1	$\cdot 035_2$	$0{\cdot}30_7$	$\cdot 3176_4$	$\cdot 3187_9$	$1{\cdot}0036_2$	$\cdot 0_3 987$	$\cdot 0_2 1001$	10336	10373	9675	9640	$-\ \cdot 36_2$	$-1{\cdot}17$
2	$\cdot 052_1$	$0{\cdot}45_4$	$\cdot 3176_0$	$\cdot 3191_8$	$1{\cdot}0049_7$	$\cdot 0_3 987$	$\cdot 0_2 1006$	10336	10387	9675	9627	$-\ \cdot 49_6$	$-1{\cdot}09$
3	$\cdot 076_2$	$0{\cdot}66_4$	$\cdot 3176_3$	$\cdot 3197_4$	$1{\cdot}0066_4$	$\cdot 0_3 987$	$\cdot 0_2 1013$	10336	10405	9675	9611	$-\ \cdot 66$	$-\ \cdot 99$
4	$\cdot 106$	$0{\cdot}92_2$	$\cdot 2984_1$	$\cdot 3008_6$	$1{\cdot}0082_1$	$\cdot 0_3 987$	$\cdot 0_2 1019$	10336	10421	9675	9596	$-\ \cdot 81_6$	$-\ \cdot 88$
5	$\cdot 136$	$1{\cdot}18_4$	$\cdot 2982_6$	$\cdot 3012_7$	$1{\cdot}0100_9$	$\cdot 0_3 987$	$\cdot 0_2 1023$	10336	10440	9675	9578	$-1{\cdot}00_2$	$-\ \cdot 84$
6	$\cdot 212$	$1{\cdot}84_9$	$\cdot 2981_4$	$\cdot 3017_3$	$1{\cdot}0120_4$	$\cdot 0_3 987$	$\cdot 0_2 1035$	10336	10461	9675	9560	$-1{\cdot}19$	$-\ \cdot 64$
7	$\cdot 262$	$2{\cdot}29$	$\cdot 2980_8$	$\cdot 3015_4$	$1{\cdot}0116_1$	$\cdot 0_3 987$	$\cdot 0_2 1028$	10336	10456	9675	9564	$-1{\cdot}14_7$	$-\ \cdot 50$
8	$\cdot 297$	$2{\cdot}59$	$\cdot 2980_8$	$\cdot 3016_8$	$1{\cdot}0120_8$	$\cdot 0_3 987$	$\cdot 0_2 1037$	10336	10461	9675	9559	$-1{\cdot}19_8$	$-\ \cdot 46$
9	$\cdot 354$	$3{\cdot}08$	$\cdot 3178_2$	$\cdot 3218_8$	$1{\cdot}0127_7$	$\cdot 0_3 987$	$\cdot 0_2 1038$	10336	10468	9675	9553	$-1{\cdot}26_1$	$-\ \cdot 41$
10	$\cdot 458$	$3{\cdot}99$	$\cdot 3177_7$	$\cdot 3212_1$	$1{\cdot}0108_3$	$\cdot 0_3 987$	$\cdot 0_2 1037$	10336	10448	9675	9571	$-1{\cdot}07_4$	$-\ \cdot 27$
11	$\cdot 604$	$5{\cdot}27$	$\cdot 3176_0$	$\cdot 3198_8$	$1{\cdot}0071_8$	$\cdot 0_3 993$ 78·4° to 100° C.	$\cdot 0_2 1023$ 78·4° to 100° C.	10336	10410	9675	9606	$-\ \cdot 71_3$	$-\ .13_5$

Table V.

Results for Eleven Dilute Liquid Sodium Amalgams at Constant Temperature 185° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $^{m}R_{t}$.	Resistance in ohms. $^{a}R_{t}$.	Relative resistivity or ratio $\frac{^{a}R_{t}}{^{m}R_{t}}$.	Average temperature coefficient of Mercury from 0° to 185° C., $= {}^{m}\alpha_{t}$.	Average temperature coefficient of Amalgam from 0° to 185° C., $= {}^{a}\alpha_{t}$.	Resistivity of Mercury at 185° C., $^{m}\rho_{t}$.	Resistivity of Amalgam at 185° C., $^{a}\rho_{t}$.	Conductivity of Mercury at 185° C., $^{m}L_{t}$.	Conductivity of Amalgam at 185° C., $^{a}L_{t}$.	$\frac{\Delta L}{L} \times 10^{2}$.	$\frac{1}{C} \cdot \frac{\Delta L}{L} \times 10^{2}$.
1	$\cdot 035_{2}$	$\cdot 30_{7}$	$\cdot 3465_{0}$	$\cdot 3478_{9}$	$1\cdot 0040_{2}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1086$	11278	11323	8867	8831	$-\cdot 40_{6}$	$-1\cdot 32$
2	$\cdot 052_{1}$	$\cdot 45_{4}$	$\cdot 3464_{6}$	$\cdot 3483_{5}$	$1\cdot 0054_{5}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1089$	11278	11340	8867	8819	$-\cdot 54_{1}$	$-1\cdot 19$
3	$\cdot 076_{2}$	$\cdot 66_{4}$	$\cdot 3464_{8}$	$\cdot 3490_{3}$	$1\cdot 0073_{6}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1094$	11278	11361	8867	8802	$-\cdot 73_{3}$	$-1\cdot 10$
4	$\cdot 105_{7}$	$\cdot 92_{2}$	$\cdot 3255_{3}$	$\cdot 3287_{0}$	$1\cdot 0097_{4}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1104$	11287	11388	8867	8781	$-\cdot 96_{9}$	$-1\cdot 05$
5	$\cdot 135_{7}$	$1\cdot 18_{4}$	$\cdot 3253_{7}$	$\cdot 3293_{8}$	$1\cdot 0123_{2}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1111$	11278	11417	8867	8759	$-1\cdot 21_{8}$	$-1\cdot 03$
6	$\cdot 212$	$1\cdot 84_{9}$	$\cdot 3252_{3}$	$\cdot 3297_{4}$	$1\cdot 0138_{6}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1114$	11278	11434	8867	8746	$-1\cdot 36_{4}$	$-\cdot 74$
7	$\cdot 262$	$2\cdot 29$	$\cdot 3251_{7}$	$\cdot 3298_{6}$	$1\cdot 0144_{2}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1117$	11278	11441	8867	8741	$-1\cdot 42_{1}$	$-\cdot 62$
8	$\cdot 297$	$2\cdot 59$	$\cdot 3251_{7}$	$\cdot 3297_{4}$	$1\cdot 0140_{5}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1117$	11278	11436	8867	8744	$-1\cdot 38_{7}$	$-\cdot 53$
9	$\cdot 354$	$3\cdot 08$	$\cdot 3467_{0}$	$\cdot 3516_{0}$	$1\cdot 0141_{3}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1113$	11278	11437	8867	8743	$-1\cdot 39_{8}$	$-\cdot 45$
10	$\cdot 456$	$3\cdot 99$	$\cdot 3466_{5}$	$\cdot 3502_{5}$	$1\cdot 0103_{8}$	$\cdot 0_{2}1075$	$\cdot 0_{2}1102$	11278	11395	8867	8776	$-1\cdot 02_{6}$	$-\cdot 26$
11	$\cdot 604$	$5\cdot 27$	$\cdot 3461_{6}$	$\cdot 3483_{4}$	$1\cdot 0054_{3}$	$\cdot 0_{2}1074$ 78·4° to 185° C.	$\cdot 0_{2}1063$ 78·4° to 185° C.	11278	11339	8867	8819	$-\cdot 54_{1}$	$-\cdot 10_{3}$

Table VI.

Dilute Sodium Amalgams at a Constant Temperature of 225·8° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $_{m}R_{t}$.	Resistance in ohms. $_{a}R_{t}$.	Relative resistivity or ratio $\frac{{}_{a}R_{t}}{{}_{m}R_{t}}$.	Average temperature coefficient of resistivity of Hg from 0° to 225·8° C., = $_{m}\alpha_{t}$.	Average temperature coefficient of resistivity of Amalgam from 0° to 225·8° C., = $_{a}\alpha_{t}$.	Resistivity of Mercury at 225·8° C., $_{m}\rho_{t}\times10^{8}$.	Resistivity of Amalgam at 225·8° C. $_{a}\rho_{t}\times10^{8}$.	Conductivity of Mercury at 225·8° C., $_{m}L_{t}$.	Conductivity of Amalgam at 225·8° C., $_{a}L_{t}$.	$\frac{\Delta L}{L}\times10^{2}$.	$\frac{1}{C}\cdot\frac{\Delta L}{L}\times10^{2}$.
1	$\cdot035_{2}$	$\cdot30_{7}$	$\cdot3619_{4}$	$\cdot3637_{4}$	$1\cdot0049_{7}$	$\cdot0_{2}1118$	$\cdot0_{2}1133$	11782	11841	8488	8446	$-\cdot49_{5}$	$-1\cdot61$
2	$\cdot052_{1}$	$\cdot45_{4}$	$\cdot3619_{0}$	$\cdot3642_{0}$	$1\cdot0063_{5}$	$\cdot0_{2}1118$	$\cdot0_{2}1135$	11782	11857	8488	8434	$-\cdot63_{6}$	$-1\cdot40$
3	$\cdot076_{2}$	$\cdot66_{4}$	$\cdot3619_{2}$	$\cdot3647_{7}$	$1\cdot0078_{7}$	$\cdot0_{2}1118$	$\cdot0_{2}1138$	11782	11875	8488	8421	$-\cdot78_{9}$	$-1\cdot19$
11	$\cdot604$	5·27	$\cdot3619_{0}$	$\cdot3630_{2}$	$1\cdot0031_{0}$	$\cdot0_{2}1115$ 78·4° to 225·8° C	$\cdot0_{2}1088$ 78·4° to 225·8° C.	11782	11819	8488	8461	$-\cdot31_{9}$	$-\cdot060$

Table VII.

Dilute Sodium Amalgams at a Constant Temperature of 255·2° C.

No. of Amalgam.	Concentration. % weight "η."	Concentration. Atomic % "C."	Resistance in ohms. $_mR_t$.	Resistance in ohms. $_aR_t$.	Relative resistivity or ratio $\frac{_aR_t}{_mR_t}$.	Average temperature coefficient of resistivity of Hg from 0° to 255·2° C., = $_ma_t$.	Average temperature coefficient of resistivity of Amalgam from 0° to 255·2° C., = $_aa_t$.	Resistivity of Mercury at 255·2° C., $_m\rho_t \times 10^8$.	Resistivity of Amalgam at 255·2° C., $_a\rho_t \times 10^8$.	Conductivity of Mercury at 225·2° C., $_mL_t$.	Conductivity of Amalgam at 255·2° C., $_aL_t$.	$\frac{\Delta L}{L} \times 10^2$.	$\frac{1}{C} \cdot \frac{\Delta L}{L} \times 10^2$.
1	$\cdot 035_2$	$\cdot 30_7$	$\cdot 3737_3$	$\cdot 3759_6$	$1 \cdot 0059_7$	$\cdot 0_2 1149$	$\cdot 0_2 1168$	12167	12240	8219	8170	$- \cdot 59_6$	$-1 \cdot 94$
2	$\cdot 052_1$	$\cdot 45_4$	$\cdot 3736_8$	$\cdot 3766_9$	$1 \cdot 0080_5$	$\cdot 0_2 1149$	$\cdot 0_2 1174$	12167	12265	8219	8153	$- \cdot 80_3$	$-1 \cdot 77$
3	$\cdot 076_2$	$\cdot 66_4$	$\cdot 3737_1$	$\cdot 3775_9$	$1 \cdot 0103_8$	$\cdot 0_2 1149$	$\cdot 0_2 1180$	12167	12293	8219	8134	$-1 \cdot 03_4$	$-1 \cdot 56$
11	$\cdot 604$	5·27	$\cdot 3936_9$	$\cdot 3765_0$	$1 \cdot 0075_2$	$\cdot 0_2 1145$ (78·4° to 255·2° C.)	$\cdot 01152$ (78·4° to 255·2° C.)	12167	12259	8219	8158	$- \cdot 74_2$	$- \cdot 14$

Table VIII.

Dilute Sodium Amalgams at a Constant Temperature of 302·2° C.

No. of Amalgam.	Concentration: % weight "η."	Concentration: Atomic % "C."	Resistance in ohms: $_{m}R_{t}$.	Resistance in ohms: $_{a}R_{t}$.	Relative resistivity or ratio $\frac{{}_{a}R_{t}}{{}_{m}R_{t}}$.	Average temperature coefficient of resistivity of Hg from 0° to 302·2° C., = $_{m}\alpha_{t}$.	Average temperature coefficient of resistivity of Amalgam from 0° to 302·2° C., = $_{a}\alpha_{t}$.	Resistivity of Mercury at 302·2° C., $_{m}\rho_{t}\times10^{8}$.	Resistivity of Amalgam at 302·2° C., $_{a}\rho_{t}\times10^{8}$.	Conductivity of Mercury at 302·2° C., $_{m}L_{t}$.	Conductivity of Amalgam at 302·2° C., $_{a}L_{t}$.	$\frac{\Delta L}{L}\times10^{2}$.	$\frac{1}{C}\cdot\frac{\Delta L}{L}\times10^{2}$.
10	·458	3·99	$·3939_{0}$	$·4001_{0}$	$1·0157_{4}$	$·0_{2}1200$	$·0_{2}1243$	12819	13021	7801	7680	$-1·55$	$-·39$
11	·604	5·27	$·3936_{7}$	$·4001_{1}$	$1·0163_{6}$	$·0_{2}1192$ 78·2° to 302·2° C.	$·0_{2}1248$ 78·4° to 302·2° C.	12819_{6}	13029	7801	7675	$-1·61_{5}$	$-·30_{7}$

Experimental Results.

The electrical resistances of pure mercury and eleven dilute sodium amalgams were measured at various temperatures, and the results are given in Tables I. to VIII.

The relative resistivity $\left(\frac{{}_a\mathrm{R}_t}{{}_m\mathrm{R}_t}\right)$ of an amalgam of a given concentration is readily obtained from measurements of the resistances of the amalgam and mercury columns under identical conditions. From the relative resistivity, the absolute resistivity ${}_a\rho_t$ and the absolute conductivity ${}_a\mathrm{L}_t$ of the amalgam can be calculated as previously explained. The values of ${}_a\bar{\alpha}_t$, the average temperature coefficient over the temperature range 0 to $t°$ C., and of $\frac{\Delta\mathrm{L}}{\mathrm{L}}\times 10^2$ and $\frac{\mathrm{I}}{\mathrm{C}}\frac{\Delta\mathrm{L}}{\mathrm{L}}\times 10^2$, have been calculated, and are included in the Tables.

The resistances were measured by means of two pyrex four-electrode tubes, and before one of the tubes was broken measurements of the resistances of mercury and amalgams 9, 10, 1, 2, 3, and 11 were completed in the order named. The second tube was then employed to measure the resistances of mercury and of amalgams 4, 5, 6, 7, and 8, in the order named. Since, as previously mentioned, the resistance of mercury was determined before and after each amalgam determination, the mercury resistances as recorded in the Tables show the effect of the chemical action of the amalgam on the diameter of the capillary tube.

Discussion of Results.

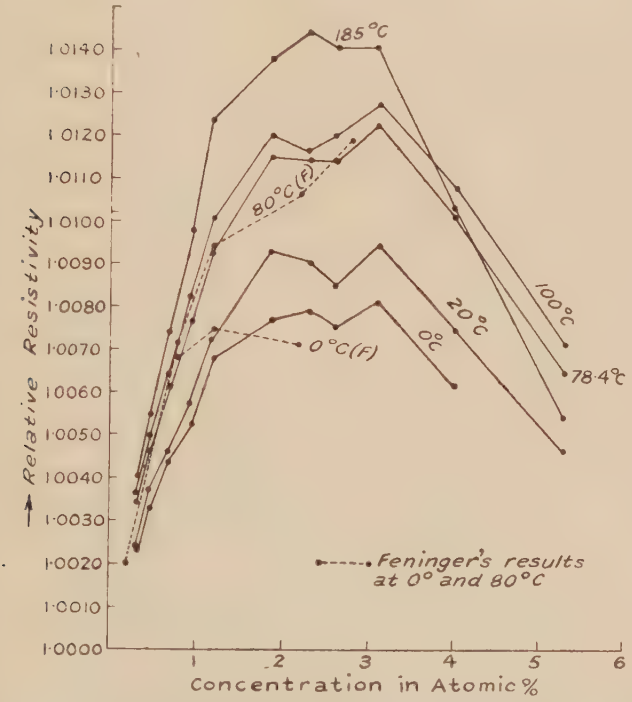
(*a*) The variation of relative resistivity at constant concentration with temperature.

This problem can be studied by reference to Graph I. It is seen that over the temperature range $0°-185°$ C., when the concentration is less than 3·6 atoms per cent., the relative resistivity increases with temperature. This result, however, does not hold for a sodium amalgam of concentration above 3·6 atoms per cent. at a temperature of 185° C.

(*b*) The variation of relative resistivity at constant temperature with concentration.

An inspection of the curves in Graph I. shows that all of them possess the same general characteristics. The value of the relative resistivity at first increases with the concentration, then remains fairly constant over a certain range of concentration, and finally diminishes with

Graph I.

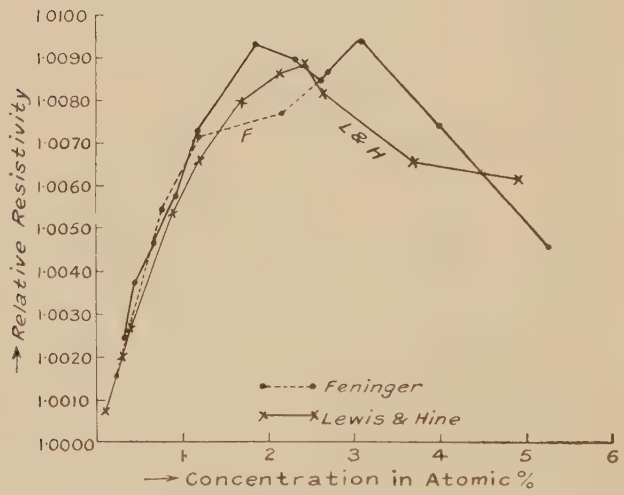


Relative resistivity-concentration curves at 0°, 20°, 78·4°, 100°, and 185° C.

further increase of concentration. The initial rise of the relative resistivity-concentration curve is steeper than the final fall. The results at higher temperatures are incomplete, but an examination of Tables VI., VII., and VIII. indicates that the general shape of the curves is, in all probability, very similar to those shown in Graph I.

Another interesting feature of these curves is the presence of discontinuities, which are specially noticeable at concentrations of 1·18, 1·85, 2·3, 2·6, and 3·08 atoms per cent. of sodium. It is difficult to decide with certainty whether these discontinuities in the curves are real, owing to the experimental difficulties encountered in the measurements, but their appearance in all the curves at practically the same concentrations seems to support the view that

Graph II.



Relative resistivity-concentration curve at 20° C. compared with results of Feninger and Lewis and Hine.

they are not altogether due to experimental errors. The results obtained in the present investigation can be compared with those of Lewis and Hine * at 20° C. and those of Feninger † at 0°, 20°, and 80° C. by reference to Graphs I. and II.

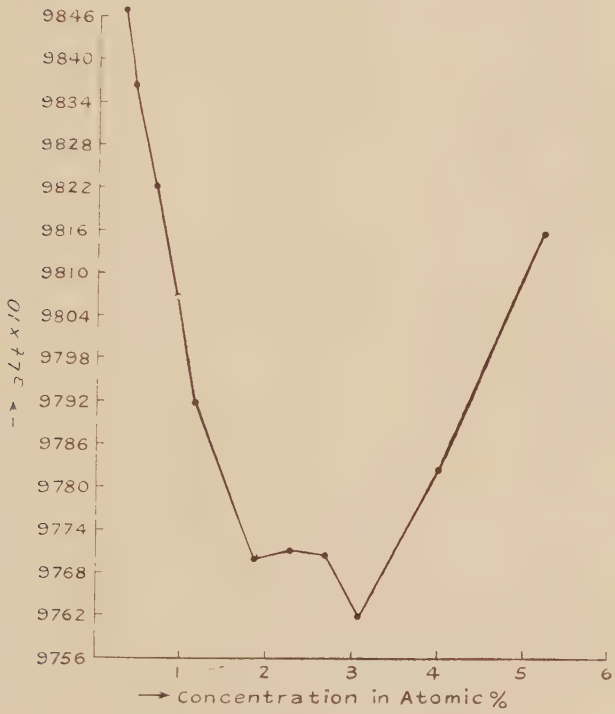
It is seen that, on the whole, the results are in fairly good agreement, and Lewis and Hine's * curve shows the same initial rise to a maximum followed by a more gradual fall.

* *Loc. cit.* † *Loc. cit.*

The Variation of Resistivity and Conductivity with Concentration at Constant Temperature, and a Comparison with Mercury.

The experimental work has shown that the resistivities of all the amalgams examined, with one exception, are greater than that of mercury at the same temperature. The exception referred to is that of an amalgam of

Graph III.



Conductivity-concentration curve at 78·4° C.

concentration 0·604 per cent. by weight (5·27 atoms per cent.) at 0° C., and its resistivity is 9376×10^{-8}, as compared with 9407×10^{-8} for pure mercury. It is, however, important to note that in the neighbourhood of 0° C. a solid mass, which seemed to possess a crystalline structure, separated from the liquid amalgam, and the measured resistivity is therefore not that of a pure liquid amalgam.

The solubility of the alkali metals in mercury increases with increasing temperature, and according to W. Kerp * and his co-workers the percentage solubility of sodium in mercury at 0°, 25°, 65°, and 100° C. is given by 0·54, 0·65, 0·86, and 1·11 respectively.

The amalgam of concentration 0·604 per cent. by weight

Graph IV.

Conductivity-concentration curve at 100° C.

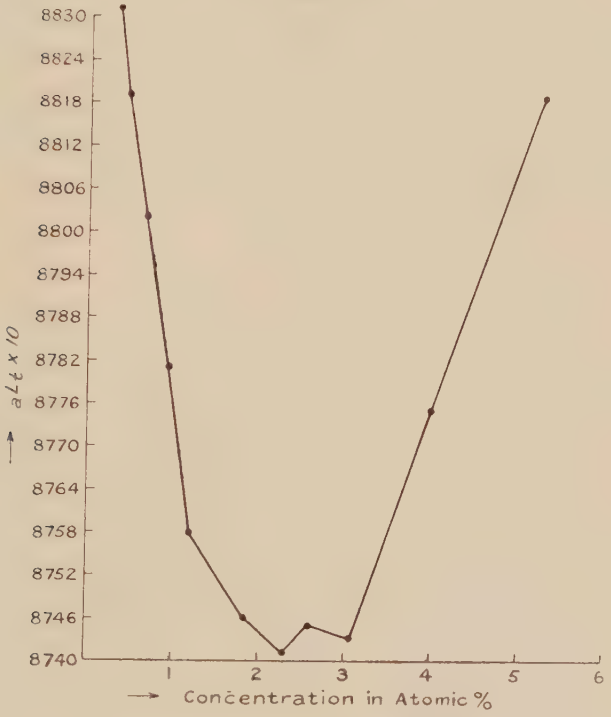
is, therefore, a liquid amalgam at all the other temperatures employed in this investigation.

An examination of Tables I.–VIII. shows that the difference between the resistivity of a sodium amalgam and mercury at the same temperature increases to a maximum as the concentration increases, and finally

* Mellor, 'Inorganic & Theoretical Chem.,' iv. p. 1010.

diminishes at the highest concentrations. A curve showing the relation between the difference of resistivity and the concentration of the sodium would be similar to the relative resistivity-concentration curve at the same temperature. The relation between the absolute conductivity and concentration is shown in Graphs III., IV., and V. which represent the experimental results at 78·4° 100°,

Graph V.



Conductivity-concentration curve at 185° C.

and 185° C. respectively. The three curves have the same form, and show at first a diminution in conductivity with increase of concentration until a minimum is reached, and a further increase of concentration is accompanied by an increase in the conductivity. The initial and final portions of the curves are approximately straight lines, but the middle portions in the neighbourhood of the minima show the presence of discontinuities.

Booharwalla, Paranjpe and Prasad *, in their experiments on the conductivities of sodium amalgams at 30° C., found two distinct discontinuities in the conductivity-concentration curve corresponding to concentrations of 0·079 and 0·272 per cent. by weight. They also found that a sodium amalgam of concentration 0·272 per cent. by weight was a better conductor than pure mercury. The present experiments also indicate the presence of a discontinuity for a concentration of 0·262 per cent. by weight (2·29 atoms per cent.) at a temperature of 20° C.; but there is no evidence of a definite discontinuity at a concentration of 0·079 per cent. by weight.

Although in the present investigation no experiments were carried out at 30° C., an examination of the relative resistivity-concentration curves at 0°, 20°, and 78·4° C. (graph I.) seems to indicate that the conductivity of the 0·272 per cent. amalgam is less than that of mercury at the same temperature.

Resistivity and Temperature.

An examination of the experimental results given in Tables I. to VIII. shows that the average temperature coefficient of resistivity of an amalgam is, in almost all cases, greater than the average temperature coefficient of pure mercury over the same range of temperature, and also that the average temperature coefficient of an amalgam of given concentration increases with the range of temperature †. The variation of the average temperature coefficient of resistivity with concentration, when the interval of temperature is kept constant, is somewhat irregular; but the general tendency is for the average temperature coefficient to increase with concentration.

In the case of amalgams of metals not belonging to Group I. of the Periodic Table the average temperature coefficient of resistivity is less than that of mercury over the same temperature range, and diminishes with increase of concentration.

Müller ‡, and later Bornemann and Rauschenplatt §, determined the resistivities of a sodium amalgam of

* *Loc. cit.*

† Mellor, 'Inorganic & Theoretical Chem.,' iv. p. 1017.

‡ *Loc. cit.*

§ The only exception is the amalgam of concentration 5·27 gram atoms per cent.

concentration 0·96 atom per cent. at temperatures up to 300° C., and the latter investigators found that the resistivity of the amalgam increased from 9976×10^{-8} at 50° C. to 13142×10^{-8} at 300° C.

The value obtained by them at 100° C. was 10274×10^{-8}, which is lower than their value for pure mercury. The resistivities of this amalgam at other temperatures is, according to their measurements, greater than the corresponding values for mercury. The resistivities obtained in the present investigation for amalgams of concentrations 0·922 and 1·184 atoms per cent. were 10421×10^{-8} and 10440×10^{-8} respectively at 100° C., and were greater than the corresponding value for mercury (10336×10^{-8})).

The Variation of $\frac{1}{C}\frac{\Delta L}{L}$ *with Temperature and Concentration.*

As already indicated, the resistivity of all the amalgams examined, with one exception, is greater than that of mercury at the same temperature, and it therefore follows that $\frac{\Delta L}{L}$ and $\frac{1}{C}\frac{\Delta L}{L}$ are negative quantities. In the case of amalgams of metals not belonging to Group I. of the Periodic Table $\frac{1}{C}\frac{\Delta L}{L}$ is positive, and increases with increase of temperature (concentration constant), but diminishes with increase of concentration (temperature constant) especially at high temperatures. An examination of Tables I. to VIII. shows that the negative value of $\frac{1}{C}\frac{\Delta L}{L}$ (concentration constant) increases with increase of temperature *. The Tables also show that the negative value of $\frac{1}{C}\frac{\Delta L}{L}$ (temperature constant) diminishes with increase of concentration. The values of $\frac{1}{C}\frac{\Delta L}{L}$ at infinite dilution or l_x are more difficult to calculate, owing to the somewhat irregular nature of the curves connecting l with concentration at constant temperature.

* The behaviour of the sodium amalgam of concentration 5·27 gram atoms per cent. is, however, rather irregular.

However, by plotting $\frac{1}{C}\frac{\Delta L}{L}$ against the concentration C at 0°, 20°, 100°, 225·8°, and 252·2° C. for the three or four lowest concentrations, it is found that the points lie approximately on straight lines, and the values of l_∞ as determined from the graphs are :—

$-0{\cdot}88\times10^{-2}$, $-0{\cdot}92\times10^{-2}$, $-1{\cdot}28\times10^{-2}$, $1{\cdot}91\times10^{-2}$, and $-2{\cdot}265\times10^{-2}$ respectively.

The values of $l_\infty - l$ and $\frac{l_\infty - l}{C}$ have also been calculated for the three temperatures 100°, 225·8°, and 255·2° C., and the results are given in the following tables :—

Temperature 100° C.

$(l_\infty - l)\times10^{-2}$.	C.	$\frac{(l_\infty - l)}{C}\times10^{-2}$.
−0·11	0·307	−0·36
−0·19	0·454	−0·42
−0·29	0·664	−0·44
−0·40	0·922	−0·43
−0·44	1·184	−0·38
−0·64	1·849	−0·34
−0·78	2·29	−0·34
−0·82	2·59	−0·32
−0·87	3·08	−0·28
−1·01	3·99	−0·25
−1·14	5·27	−0·22

Temperature 225·8° C.

$(l_\infty - l)\times10^{-2}$.	C.	$\frac{(l_\infty - l)}{C}\times10^{-2}$.
−0·30	0·307	−0·98
−0·51	0·454	−1·12
−0·72	0·664	−1·08

Temperature 255·2° C.

$(l_\infty - l)\times10^{-2}$.	C.	$\frac{(l_\infty - l)}{C}\times10^{-2}$.
$-0{\cdot}32_5$	0·307	−1·06
$-0{\cdot}49_5$	0·454	−1·09
$-0{\cdot}70_5$	0·664	−1·07

The above tables indicate that, in the case of the most dilute solutions, the value of $\frac{l_\infty - l}{C}$ is approximately constant at each of the three temperatures. The figures given in the first table (100° C.) also show that for concentrations greater than about 1·0 atom per cent. the negative value of $\frac{l_\infty - l}{C}$ diminishes continuously with increase of concentration, and it is interesting to note that the discontinuities in the conductivity-concentration curves commence at a concentration of about 1 atom per cent.

According to Skaupy's * hypothesis the value of $H_\infty = l_\infty + r_\infty$, where $r = \frac{1}{C}\frac{\Delta\eta}{\eta}$, should be constant for all metals dissolved in mercury, and also $H_\infty - H$ should vary linearly with the concentration C.

Feninger † gives the values of the viscosity at 18° C. of two sodium amalgams of concentrations 0·311 and 0·482 atoms per cent. Assuming that $\frac{1}{C}\frac{\Delta\eta}{\eta}$ varies linearly with concentration, the calculated value of $\frac{1}{C}\cdot\frac{\Delta\eta}{\eta}$ at infinite dilution for a temperature of 18° C. is $9{\cdot}3\times10^{-2}$.

Since the value of $\frac{1}{C}\frac{\Delta L}{L}$ at infinite dilution (temperature 20° C.) is $-0{\cdot}92\times10^{-2}$, it follows that H_∞ has the value $8{\cdot}4\times10^{-2}$, which is of the same order of magnitude as the value of H ($9{\cdot}8\times10^{-2}$) for gold amalgams at room temperature.

This latter value was calculated from Feninger.s viscosity measurements and Williams and Evan's ‡ conductivity measurements. It is, however, impossible to consider the problem further, owing to lack of data on the viscosity of sodium amalgams over a wide range of temperature.

In the relation $\frac{H_\infty - H}{C}$ = constant, H is the value of $l+r$ at concentration C. From Feninger's § results for sodium amalgams of concentrations 0·311 and 0·482 at

* *Loc. cit.*
† *Loc. cit.*
‡ *Loc. cit.*
§ *Loc. cit.*

18° C. the calculated values of r are $10{\cdot}3 \times 10^{-2}$ and $11{\cdot}1 \times 10^{-2}$ respectively.

The values of l at 20° C. for the same concentrations can be obtained by plotting the first four values of $\frac{1}{C}\frac{\Delta L}{L}$ in Table II. against the concentration. The values thus obtained for the two concentrations 0·311 and 0·482 are $-0{\cdot}82 \times 10^{-2}$ and $-0{\cdot}77 \times 10^{-2}$ respectively. Since $H_\infty = 8{\cdot}4 \times 10^{-2}$, it follows that the values of $\frac{H_\infty - H}{C}$ for the sodium amalgams of the above concentrations are $-3{\cdot}5 \times 10^{-2}$ and $-4{\cdot}0 \times 10^{-2}$ respectively.

Although the values are in fair agreement, considering the possible experimental errors, more experimental data relating to the viscosities of sodium amalgams at various temperatures must be available before the truth of the equation $\frac{H_\infty - H}{C} = \text{constant}$ can be verified.

The physical properties of alkali amalgams have been studied by a large number of chemists *, and the general results seem to indicate that in all probability amalgams are solutions of compounds of the dissolved metal with definite proportions of the solvent mercury in excess of mercury. Several compounds of sodium with mercury are supposed to exist, and some of them are considered to have been isolated. A comparison of the experimental results obtained for the conductivities of sodium amalgams with those obtained by Williams and Evans † for the amalgams of copper, silver, and gold show that the sodium amalgams behave in a more complicated manner than the latter. The small discontinuities in the conductivity-concentration curves are not unlike the discontinuities in similar curves obtained with alloys due to the production of intermetallic compounds, but the magnitudes of the changes in conductivity are much less.

The discontinuities, together with the fact that large amounts of heat are evolved during the production of sodium amalgams, may possibly be regarded as lending support to the view that compounds of mercury and sodium exist even in moderately dilute sodium amalgams.

* Mellor, 'Inorganic and Theoretical Chemistry,' iv. p. 1017.
† *Loc. cit.*

Summary of Results.

1. The electrical resistivities of eleven liquid sodium amalgams of concentrations ranging from 0·307 to 5·27 atoms per cent. were measured at 0°, 20°, 78·4°, 100°, and 185° C. In the case of a few of these amalgams, measurements were also carried out at 225·8°, 255·2°, and 302·2° C.

2. It was found that the relative resistivity of an amalgam (*i. e.*, its resistivity relative to mercury) at constant temperature at first increases with increase in the concentration of the sodium, then remains practically constant over a certain range of concentration, and finally diminishes with further increase of concentration. The relative resistivity-concentration curves in the neighbourhood of the maxima are somewhat irregular, and seem to show the presence of small discontinuities.

3. The absolute conductivity of an amalgam at constant temperature at first diminishes with increase in the concentration of the sodium, then remains fairly constant over a certain range of concentration, and finally increases with further increase of concentration. Discontinuities also appear on the conductivity-concentration curves in the neighbourhood of the minima.

4. The average temperature coefficient of resistivity of the sodium amalgams examined in this investigation is generally greater than the average temperature coefficient of resistivity of pure mercury over the same range of temperature.

For an amalgam of a given concentration the average temperature coefficient increases with the temperature range.

5. The variation of the average temperature coefficient of resistivity with concentration is somewhat irregular, but the general tendency is for the average temperature coefficient to increase with concentration.

6. The variation of $\frac{1}{C}\frac{\Delta L}{L}$ with temperature and concentration has been considered, and the results examined in relation to a theory put forward by Skaupy *.

* *Loc. cit.*

LIX. *Some Precision Measurements in the Soft X-ray Region.* *By* M. Söderman *.

[Plates III. & IV.]

DURING the last ten years a great many researches have been made in order to join the ultra-violet and the soft X-ray region. Millikan and his assistants †, working from the ultra-violet side and using concave gratings, succeeded in registering wave-lengths down to 136 Å. Later researches in this region have been carried out by Léon and Eugène Bloch, Lyman, Wood, and others. Last year Edlén and Ericson ‡, of this laboratory, reached down to 75 Å., and this record was recently surpassed by Ekefors §, also working here, who found spark-lines from aluminium below 50 Å.

Indirect Methods.

The first attempts to attain greater wave-lengths from the X-ray side were made by indirect methods. Their aim is to determine the critical potentials of the elements. This is done by placing the element to be examined on the anode and bombarding it with an electron current from a tungsten filament. The accelerating potential is raised by steps, and the excited radiation is measured by the photo-electric effect produced upon an electrode, which is protected from the corpuscular radiation. In order to estimate where the discontinuities are to be found, the authors plot the photoelectric current as a function of the tension. Along the row of points thus obtained they place straight lines, and from the points of intersection of these lines they purport to be able to estimate the values of critical potentials with rather high accuracy. A great many researches have been carried out by this method ||.

* Communicated by Dr. Manne Siegbahn.

† R. A. Millikan, I. S. Bowen, and R. A. Sawyer, Astrophys. Journ. liii. p. 150 (1921); R. A. Millikan and I. S. Bowen, Phys. Rev. xxiii. p. 1 (1924).

‡ Bengt Edlén and Algot Ericson, *Zs. für Physik*, lix. p. 656 (1930).

§ E. Ekefors, *Phys. Zs.* xxxi. p. 737 (1930).

|| E. H. Kurth, Phys. Rev. (2) xviii. p. 99 (1921); A. Ll. Hughes, Phil. Mag. xliii. p. 145 (1922); J. Holtsmark, *Phys. Zs.* xxiii. p. 252 (1922); J. C. McLennan and M. L. Clark, Proc. Roy. Soc. (A), cii. p. 389 (1923); M. Levi, Roy. Soc. Canada, xviii. p. 159 (1924); Charles Thomas, Phys. Rev. xxv. p. 322 (1925); G. K. Rollefson, Phys. Rev. xxv. p. 740 (1925).

but the agreement among the results obtained by different observers is very bad. Moreover, when repeated the investigations in this region would give new discontinuities besides those already observed, and a comparison of all the discontinuities that have been found shows that they are practically evenly distributed over the whole region examined, except possibly the value at about 290 volts, which has been obtained by most observers and is regarded as the K-absorption limit of carbon, due to the presence of hydrocarbon vapours from the vacuum grease. The other results of the examinations made by this method are so doubtful that a comparison of them with the results obtained by more reliable methods would hardly be of any interest.

A method that is better in principle has been worked out by Mohler and Foote *. The element to be examined is in its gaseous state, and, as in the experiments described above, the variation of the photo-electric current is used for the determination of the critical potentials. The values obtained for the K-limit are given in Table I.

Table I.

Element.	4 Be.	5 B.	6 C.	7 N.	8 O.
K-limit (volts)	116	186	272	374	478

A comparison with the results obtained by the grating method (Table IX., p. 616) shows that the critical potentials for boron and beryllium might be rather good, but the values found for carbon, nitrogen, and oxygen must be too low, their energies being even less than those of the K_α radiation.

According to the method introduced by Richardson and Bazzoni † the radiation that is to be examined produces photo-electrons, and their velocity is determined by their deviation in a magnetic field. A somewhat modified application of this method has been made by Lukirsky ‡, who, instead of deflecting the photo-electrons, determines

* F. L. Mohler and P. D. Foote; Scient. Pap. Bur. of Stand. xvii. p. 471 (1922).

† O. W. Richardson and C. B. Bazzoni, Phil. Mag. xlii. p. 1015 (1921).

‡ P. Lukirsky, Phil. Mag. xlvii. p. 466 (1924).

their stopping potentials by means of an electric field. The most complete investigation by this method was carried out by Rudberg *, who found the values shown in Table II.

Table II.

Element.	4 Be.	5 B.	6 C.
K_α (volts)	96	178	273

It is to be observed that this method gives the energy of the K_α-radiation, and not, like the two other methods, the K-limit. The critical values are determined, however, by the same plotting method, which is by no means objective and able to give reliable results. The agreement with the results obtained by the grating method is not very good, Rudberg's values being evidently too low.

The one of the indirect methods that seems to have given the best and most reliable results is the absorption method used by Holweck †. The values obtained by him, representing the K-limit, are given in Table III.

Table III.

Element.	5 B.	6 C.	7 N.	8 O.	9 F.	13 Al.
K-limit (volts) ...	192	280·5	397	528	684	1555

These results seem to agree well with those obtained in this research (Table IX., p. 616).

Among other indirect methods for studying the radiation in the intermediate region that of Rollefson and Poth ‖ is worth mentioning. Its aim is to determine the ionization potentials for the elements in the photographic emulsion. This is done by making a magnetically spread continuous cathode ray spectrum fall upon a photographic plate, and observing the places where the blackening shows irregularities.

* E. Rudberg, *Kungl. Sv. Vetenskapsakad. Handl.* ser. 3, band 7 (1929).
† F. Holweck, "De la lumière aux rayons X" (Conf. Rapp. 1927).
‡ G. K. Rollefson and E. J. Poth, 'Science,' n. s. lxii. p. 497 (1925).

Crystal Measurements.

In 1923 and 1924 the first successful attempts to extend the region of crystal spectroscopy in the direction of greater wave-lengths were made by Siegbahn and Thoræus *, who constructed a vacuum spectrograph for these wave-lengths. With this apparatus Thoræus † registered wave-lengths in the L-series up to about 25 Å. and the K-radiation from fluorine and oxygen. Some years later Dauvillier ‡ succeeded in extending the region of crystal spectroscopy to about 120 Å. His results, however, are somewhat different from those obtained with better methods. A research upon the crystal method for soft X-rays, recently carried out in this laboratory by A. Karlsson §, shows that the grating constants of the complex fatty acids used by Dauvillier are very difficult to determine, and the values obtained differ a good deal from one another. The best spectrograms in this region have been obtained with crystals of palmitic acid. Karlsson also registered some wave-lengths in the K-series, and found the values shown in Table IV.

TABLE IV.

Element.	Na.	F.	O.	N.
K_α (Å)	11·88	18·27	23·66	31·54

Greater wave-lengths than that of nitrogen proved to be impossible to measure with sufficient accuracy.

Grating Methods.

Compton and Doan || were the first who used plane gratings for X-ray purposes. Their measurements, however, are limited to wave-lengths between 1 and 2 Å. After them several investigators have used the method for

* M. Siegbahn and Thoræus, *Arkiv. för Mat. Astr. o. Fys.* Bd. xviii. no. 24, 1924, and Bd. xix. no. 12, 1925.

† R. Thoræus, Phil. Mag. (7) i. p. 312 (1926).

‡ A. Dauvillier, *Journ. de Phys.* viii. p. 1 (1927).

§ A. Karlsson, *Arkiv. för Mat. Astr. o. Fys.* Bd. xxii. A, no. 9.

|| A. H. Compton and R. L. Doan, Proc. Nat. Acad. Amer. ii. p. 598 (1925).

exploring the intermediate region. Thus Thibaud * registered several lines in the soft X-ray region as well as in ultra-violet by means of a plane grating with grazing incidence. Further, the method has been used by Bäcklin † for a precision measurement of the Al–K_α wave-length referred to absolute dimensions. For the wave-length just mentioned he finds $\lambda = 8{\cdot}333$ Å, while Larsson's precision measurement ‡ with a crystal gives $\lambda = 8{\cdot}323$ Å. Thus a certain wave-length referred to absolute dimensions becomes about 0·1 per cent. higher than when it is referred to the crystal scale, a fact which was rather unimportant as long as the accuracy of the grating measurements was about 1 per cent., but which must now be taken into consideration on a comparison between the wave-lengths found at different researches in the soft X-ray region, where both scales are used side by side. Some American investigators § have also been busy with the same problem as Bäcklin, but their results are rather different. For the electron charge which can be calculated if the relation between absolute scale and crystal scale is known the authors obtain the following values :—

Wadlund : $e = 4{\cdot}774$ E.S.U.
Bäcklin : $e = 4{\cdot}793$.
Bearden : $e = 4{\cdot}835$, $4{\cdot}824$, $4{\cdot}804$, $4{\cdot}809$ (found at different times).

Among other absolute measurements of X-ray wave-lengths those carried out by Howe ‖ should be mentioned. He has examined several lines in the L-series and the K_α-line of carbon, which he has found to be $44{\cdot}60 \pm 0{\cdot}04$ Å. Considering the fact that this wave-length is referred to the absolute scale and the one obtained by myself (Table IX.) to the crystal scale, the two results are to be regarded as well agreeing. A statement published by Bazzoni, Faust, and Weatherby ¶ is specially interesting. The

* J. Thibaud, *Journ. de Phys.* viii. p. 13 (1927), and *Phys. Zs.* xxix. p. 241 (1928).

† E. Bäcklin, "Abs. Wellenlängenbest. der Röntgenstrahlen," *Upps. Univ. Årsskr.* (1928).

‡ Not yet published.

§ A. P. R. Wadlund, Phys Rev. xxxii. p. 841 (1928); J. A. Bearden, Bull. Amer. Phys. Soc. (April 1929).

‖ C. E. Howe, Phys. Rev. xxxv. p. 717 (1930).

¶ C. B. Bazzoni, L. Y. Faust, and B. B. Weatherby, Phys. Rev. xxxiiii. p. 1101 (1929).

authors claim to have found several components in the diffuse lines C K_α and B K_α by a densitometric method. The hypothesis that the diffuseness of these lines could be explained as a fine structure was mentioned by the author in an earlier paper *, but the research that has been carried out now proves that, even when great dispersion and narrow slits are used, one single but broad line appears, the blackening curve of which varies without discontinuities, rather steep on the short wave-length side and less inclined on the other (see fig. 9, Pl. IV.), and this progress becomes finer and more uniform with improvement in the quality of the grating. The diffuseness of the K-lines from these lightest elements could possibly be explained by the assumption that the influence of the neighbouring atoms is proportionately greater than in heavier elements, or, in other words, that distinct X-ray levels do not exist in the lightest elements when they are in the solid state. Besides that it seems possible that the thermal motion of the emitting atoms could be of some influence. The observed resolution into components is probably explained in the simplest manner by the existence of focal defects in the grating.

Relative measurements with plane gratings have been carried out by Hunt †, who determined the wave-lengths of Al K_α and C K_α referred to Cu L_γ. Much greater accuracy was reached by Kellström ‡, who measured the L-series of the elements 29 Cu–20 Ca referred to Al K_α, the wave-length of which has been determined by crystal precision measurement as was mentioned above §.

The investigation of the K-series of the light elements carried out by the author was begun in the summer of 1928 as a relative measurement referred to Al K_α. A preliminary report on this work was published in January 1929 ||. Using an apparatus which permits greater accuracy in adjusting and by means of the new gratings made in this laboratory ¶ I have succeeded in increasing the accuracy of the values obtained. Also the examinations have been carried out with different angles of incidence

* M. Söderman, *Zs. für Physik*, lii. p. 795 (1929).
† F. L. Hunt, Phys. Rev. xxx. p. 227 (1927).
‡ G. Kellström, *Zs. für Physik*, lviii. p. 511 (1929).
§ Page 604.
|| *Zs. für Physik*, lii. p. 795 (1929).
¶ M. Siegbahn and T. Magnusson, *Zs. für Physik*, lxii. p. 435 (1930).

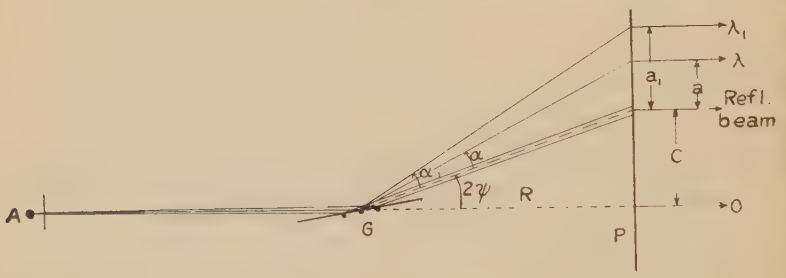
and with several gratings, ruled with 300, 900, and 1800 lines per millimetre respectively, so as to make the results more reliable. Further it has turned out to be practical to exchange the Al K_α-line for Cu L_α as reference line, the latter reaching nearly the same wave-length in its third order as the former in its fifth.

For the study of soft X-rays also concave gratings have been used. The concave grating method was tried by Osgood *, who has published some results in the region 50–200 Å. He has also given a complete synopsis of the spectroscopic methods in the region between ultra-violet and X-radiation †. It seems, however, as if the few results hitherto obtained with concave gratings in the X-ray region are rather doubtful.

The Apparatus.

The horizontal section through the apparatus, given schematically in fig. 1, shows the principle on which it is

Fig. 1.



constructed. The X-rays from the anode (A) pass a slit and fall upon the grating (G). The spectrogram is photographed on the plate (P).

The apparatus was constructed in this laboratory in the summer of 1929. Its exterior is shown in fig. 2, Pl. III. The X-ray tube is of the type usually employed here, and fitted with water-cooling both in the tube itself and in the electrodes, which permits a heavy current (250 milliamps at 4000 volts). It proved, however, to be very difficult to get good focussing when the tension was so low as in

* T. H. Osgood, Phys. Rev. (2) xxx. p. 567 (1927).
† T. H. Osgood, Phys. Rev., Suppl. (October 1929).

this investigation. This problem was solved in a simple but effective manner by means of the arrangement sketched in fig. 5. A diaphragm with a hole 2 or 3 millimetres in diameter was placed between the hot cathode and the anode, and connected with the earth. In order

Fig. 5.

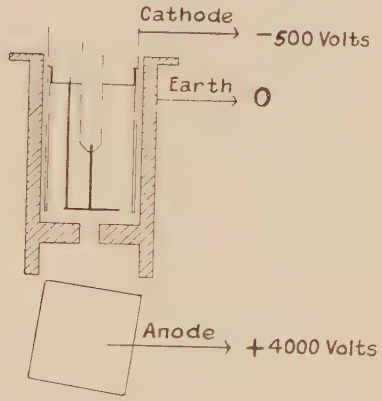
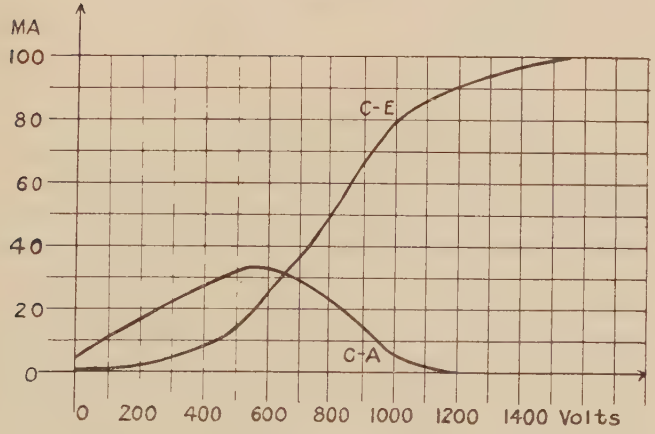


Fig. 6.



to make an electron current pass to the anode it was necessary to apply an accelerating negative auxiliary tension at the cathode. The currents in the two circuits cathode–anode (C–A) and cathode–earth (C–E) are plotted in fig. 6 as functions of the applied auxiliary

tension. The values used in this diagram are found in Table V. It is evident from the diagram that the anode current, which produces the X-radiation, could not be higher than about 35 milliamps, but of course it could have been raised by increasing the current through the hot cathode. The focus, however, was so sharp and the effect upon each superficial element so great that the current could hardly be increased further without melting the anode metal at the point of focus. The intensity of the X-radiation that passes the slit at 30 milliamps with this arrangement is greater than that procured by 250 milliamps falling upon a spread focus spot. Another great advantage is that the sputtering from the tungsten filament becomes a minimum and practically disappears when the vacuum is good.

The slit was made of tempered steel. Its width could be varied by putting in metal foils. The slit-widths used in

Table V.

Aux. tension (volts)	0	220	500	1000	1500
Current C–A (MA)	5	18	33	5	—
Current C–E (MA)	0	3	15	80	90

this investigation were between 15 μ and 50 μ. The slit could be turned in a plane at right angles to the direction of the X-ray beam by means of a lever (fig. 4, Pl. III.). A protecting slit between this slit and the grating, seen on the same figure, screened the optical beams diffracted from the first slit.

The gratings, which, as already mentioned, were produced in this laboratory, were ruled on plane glass plates. Since the ruled surface was only about 2 millimetres wide, there was no need of the usual second slit to limit the width of the diffracted beam, which was now equal to the projection of the width of the ruled surface on a plane at right angles to the beam. Also the position of the reflected beam could be easily determined, since the ruled part of the surface reflected less than the polished part on both sides, so the region on the plate corresponding to the reflected beam from the ruled surface appeared as a sharply limited

white line (C on fig. 8, Pl. IV.) upon the background, blackened by the radiation reflected from the unruled surface. In order to limit the background an edge was applied some tenth of a millimetre before the centre of the ruled surface. It is to be observed, however, that this edge serves only as a protecting screen, and does not screen off any of the lines on the grating nor the beams coming from it. In this manner the screening correction, calculated by Bäcklin * for ordinary gratings, becomes unnecessary. The best contrast between illuminated and unilluminated field on this part of the plate was obtained with very short exposures : so a steel screen was placed in the path of the reflected beam. Near the end of each exposure the screen was removed by an electromagnet and the exposure continued for about 15 or 20 seconds, after which the circuit was disconnected. The appearance of the grating-table is shown in fig. 4, Pl. III. The grating is mounted in a holder which can be placed under the microscope for adjustment. Further, the whole grating-table can be turned about a conical joint, whose position is carefully fixed in the apparatus.

The plate-holder can be adjusted by means of three screws. Its position is particularly firm, since it is connected to the apparatus with two balks, shown in fig. 3, Pl. III. Both Imperial Eclipse and Agfa Contrast plates were used. The Contrast plates required somewhat longer exposure, especially for long wave-lengths ; but the lines became sharper, which aided their measurement. In particular some of the sharpest lines had to be exposed on Contrast plates, since their whole width was of the same magnitude as the grains of the Eclipse plates. Fig. 8, Pl. IV., gives a comparison between an Eclipse plate and a Schumann plate, exposed under the same conditions. The Schumann plate is evidently less sensitive for the rather short wave-lengths (continuous radiation and Cu L_α), while the soft O K_α and C K_α lines appear with nearly the same intensity on both plates.

The whole apparatus can be hermetically shut by a steel cylinder, which rests upon a rubber gasket in the brass plate (figs. 3 and 4, Pl. III.). Though the volume amounts to 12 litres, it can be evacuated in 5 minutes by means of an oil-pump and a Siegbahn disk-pump of the smallest type.

* E. Bäcklin, *l. c.* p. 36.

The generator was capable of producing 250 milliamps at 5000 volts. For the accelerating tension (see p. 607) another high-tension generator was first used, but, as there proved to be no use in making this tension higher than about 500 volts, the second generator was replaced by a battery connected in series with the municipal direct-current lighting-system. The hot-filament current was obtained from a step-down transformer.

Adjustments and Measurements.

The grating to be used was mounted in an optical spectrometer and its grating constant determined in the usual manner. The gratings being ruled on plane parallel glass plates, they could be used for either reflexion or transmission. The determination of the dispersion for the grating with 1800 lines per millimetre is of special interest. Used as a transmitting grating, and illuminated by sunlight falling normally upon it, it gives a spectrum with very great dispersion. The beams deviated the least, *i. e.*, the violet rays in the first order, leave the grating at an angle of deviation of about 50°. The blue and green regions of the spectrum are also well visible, but in the yellowish green it makes a sudden stop, the angle of deviation being 90°. The position of this limit can be estimated by means of the absorption lines in the spectrum. The wave-length, corresponding to it, is evidently equal to the grating constant. By this method it is possible to estimate the value of the grating constant with rather high accuracy even without using the scale of the spectrometer—that is, the determination can as well be made with a spectroscope. To determine the grating constant by means of a microscope would be very difficult in this case, the distance between the ruled lines being less than the resolving power of the microscope. The only possibility for such a measurement would be the method suggested by Grossmuller and Lakemann * to observe the phenomena of interference produced by a fine fibre stretched obliquely across the ruled surface.

When the grating constant had been determined the grating was mounted in its holder and adjusted under the microscope, so that the protecting edge became parallel to

* J. Th. Grossmuller and C. Lakemann, *Zs. für Physik*, lix. p. 215 (1929).

the lines and before the middle of the ruled surface. In order to make this adjustment easy the middle of each grating ruled in this laboratory is marked by a line some millimetres longer than the others. The grating holder was fixed upon the table and its position adjusted parallel to the axis of rotation by means of a telescope and scale. Part of the surface outside the ruling was silvered, in order to make the readings easier. A surface-silvered plane glass plate was laid against the plane polished surface of the edge before the grating, and by readings in this glass the edge, and at the same time the ruled lines, could be made parallel to the axis of rotation of the grating table. After that the edge was screwed up to the grating. Then it evidently coincides with the middle line. This line had to be brought into the true axis of rotation, which was done by observing the edge through a microscope from above and adjusting by the two screws (fig. 4, Pl. III.) until the edge was stationary, when the grating table was rotated. After that the position of the whole apparatus was adjusted by its base screws, so that the axis of rotation was vertical. This was observed through a telescope, whose rotation axis could be carefully adjusted vertical, by comparing the direction of the edge with that of two plumb-lines hanging at the same distance from the telescope as the edge. In the same manner the first slit was made vertical, *i. e.*, parallel to the second.

The position of the plate-holder was adjusted by putting in a surface-silvered glass plate in the place of the photographic plate. The grating was rotated until the angle of incidence became 0°, when a beam from the first slit, which was illuminated, passed the second slit without deviation, thus marking the middle line of the apparatus. That part of the beam which came from the middle, vertically, of the ruled surface was screened off, and the position of the plate-holder adjusted until the edge of the screened beam was reflected into its own path. In order to make it possible to vary the position of the point of focus, the hole in the diaphragm, described on p. 607 was eccentrically drilled, and it could be decided by trial exposures at what position of the focus spot the emitted X-radiation reached a maximum. The distance between the grating and the plate was measured with an iron rod, whose length could be varied by a micrometer screw.

Indicating the angle of incidence by ψ, the wave-length

to be referred by by λ, and the wave-length to be measured by λ_1, we obtain, according to the grating formula,

$$\lambda = 2e \sin \frac{2\psi + \alpha}{2} \sin \frac{\alpha}{2},$$

$$\lambda_1 = 2e \sin \frac{2\psi + \alpha_1}{2} \sin \frac{a_1}{2},$$

where e denotes the grating constant, $2\psi + \alpha$ and $2\psi + \alpha_1$ the angles of deviation (fig. 1, p. 606). If the distance between the grating and the plate is denoted by R, the distance from the point O (fig. 1) to the reflected beam by C, and the distance from this to the reference line and to the unknown line by a and a_1 respectively, it is evident that

$$\tan (2\psi + \alpha) = \frac{C + a}{R},$$

$$\tan (2\psi + \alpha_1) = \frac{C + a_1}{R},$$

$$\tan 2\psi = \frac{C}{R}.$$

The exact solution of this system leads to a very complicated expression for λ_1, but, the angles in question being small, several approximations can be made. In this investigation the wave-lengths were calculated according to the approximate formula

$$\lambda_1 = \frac{a_1}{a} \cdot \lambda + \frac{e}{2R^2} a_1 (a_1 - a),$$

which gives too small values for the wave-lengths below the reference-line and too great for the others. In order to make the results coincide a correction is applied, determined by means of a graph for each dispersion, so that the value of the reference wave-length, calculated from different orders, is always the same. The total amount of this correction in no case exceeds 0·6 per cent., and the uncertainty for this greatest value of the correction is only about 0·02 per cent. Thus the errors arising from the approximation in the mathematical treatment may be neglected.

For some plates, where the reference-line appears in three orders or more, also another method of calculation

has been used. Supposing that the wave-length (λ) depends upon the line's distance (a) from the reflected beam according to the function

$$\lambda = A \cdot a + B \cdot a^2 + C \cdot a^3,$$

one may calculate the constants A, B, and C, and thus determinate the wave-length λ_1. Terms containing higher powers than a^3 can be neglected, even the term Ca^3 being very small compared with the two other terms. The advantage of this method is its purely empirical character, *i.e.*, it is not based upon any questionable assumptions about the reflexion at grazing incidence and about the constants included in the formula, but it gives directly one wave-length referred to another.

The plates have been treated one by one, and the angle of incidence has been varied between most exposures. The following values have been obtained :—

		Grating constant.	Lines/mm.
Grating 47....	$e = 33367$	± 3 Å.	299·70
,, 15....	$e = 10984$	$\pm 1{\cdot}5$,,	910·4
,, 29....	$e = 5601{\cdot}1$	± 1 ,,	1785·4

Distance between grating and plate : $R = 271{\cdot}3 \pm 0{\cdot}1$ mm.

Table VI.

O K_α.		N K_α.		C K_α.	B K_α.	Be K_α.
I.	II.	I.	II.	I.	I.	I.
23·57	23·58	31·56	31·63	44·61	67·79	115·54
55	60	54	64	50	71	84
57	58	52	59	50	63	
57	56	·54		55		
	56	52		51		
	57	52		58		
	60	51		54		
	57					
23·57		31·56		44·54	67·71	115·7

The lowest dispersion (900/3) has been used only for the elements O, N, C, B, and Be. The results calculated from different orders and different plates are shown in Table VI. All values except that for Be K have been

referred to Cu $L_\alpha = 13{\cdot}306$ Å.*, and exposed with angles of incidence between 1° and 1°·5. For the beryllium line one maximum had earlier † been found at 113·4 and one at 119 Å. It was then suspected that this maximum depended upon the line $OK_{\alpha V}$. In order to determine whether this was the case I have now worked with greater angles of incidence, 3°·5 and 4°. At these angles the intensity of the reflected O K_α-radiation becomes negligible, though no sharp "angle of total reflexion" seems to exist, a fact noticed by many other observers‡. At these great angles

Table VII.

Al K_α.		Mg K_α.			Na K_α.	F K_α.	O K_α.		N K_α.
I.	II.	I.	II.	III.	I.	I.	I.		I.
8·321	8·323	9·888	9·873	9·876	11·884	18·276	23·572	·554	31·553
322	325	879	·871		885	270	545	554	
324	324	869			885	268	540	567	
		876					555	550	
		872					572	569	
		874					572	559	
		892					555		
		875					549		
8·323		9·877			11·885	18·271	23·557		31·553

of incidence, however, no Cu L_α-lines appear, and the beryllium line had to be referred to C K_α, which appeared in four orders on both plates, and whose wave-length was taken as 44·54 Å. On these plates the blackening curve of the beryllium line proved wholly smooth, analogous to that of the carbon, but spread over a yet greater region of wave-length (see Table IX.). The fact that the value which has now been obtained for the beryllium line is greater than that found earlier is probably due to a simply physiological phenomenon. Experience has proved that

* Recently determined in this laboratory by A. Larsson.

† M. Söderman, *l. c.* p. 803.

‡ El. Laird, Phys. Rev. (2) xxvii. p. 510 (1926); H. E. Strauss, Phys. Rev. (2) xxxi. p. 491 (1928); M. Valouch, *Journ. de Phys.* (6) x. p. 109 S. (1929); J. A. Prins, 'Nature,' cxxiv. p. 370 (1929).

in comparator measurements on a diffuse line with unsymmetric blackening the comparator is set between the maximum and the middle of the line, the flatter blackening curve the nearer the middle. If a second maximum appears the two settings are made too far apart—that is, in this case the real maximum was given too short a wave-length.

The angles of incidence which were used for grating 15 (1800 '2) were 0°·8, 1°·0, and 1°·5. The values obtained are shown in Table VII.

The greatest dispersion (1800 '1) was used only for the wave-lengths of the elements Al–O. Table VIII. gives the values obtained.

Table VIII.

Al $K_{\alpha_{1,2}}$.			Mg $K_{\alpha_{1,2}}$.		Na K_{α}.	F K_{α}.	O K_{α}.
I.	II.	III.	I.	II.	I.	I.	I.
8·321	8·325	8·320	9·868	9·874	11·887	18·287	23·549
322	321	320	873	873	885	284	562
320	324		871		885	274	569
320	324		874		883		580
321	325		869		887		576
326							578
321							
324							
	8·322		9·872		11·885	18·282	23·569

With this dispersion also some other lines than the $K_{\alpha_{1,2}}$ could be measured. Thus in Al and Mg it was possible to distinguish between a strong line corresponding to $K_{\alpha_{1,2}}$ and a faint line partly overlapping the other and probably due to $K_{\alpha 3,4}$. The lines could be measured one by one and their separation was found to be 0·060 Å for Al and 0·075 Å. for Mg, in good agreement with the results obtained by crystal methods. Further, the K_{β}-line of aluminium appeared after sufficient exposure, and could be measured. Its distance from the $K_{\alpha_{1,2}}$-line was 0·370 Å.

Table IX. gives a summary of the results of this research. The mean errors of the values obtained from different orders and different plates are between 0·02 and 0·03 per

cent. for the elements Al–F, and increase gradually with increasing wave-lengths from 0·06 per cent. for O to 0·15 per cent. for Be. It might be possible to raise the accuracy a little for the wave-lengths of the first elements of the table, especially by using narrower slits, but for the lightest elements this is of no interest. The flatness of the blackening curves for these elements makes a specific indication of its maximum hardly possible; nor is it suitable to state the middle of the unsymmetric blackening as the wave-length. Taking this into consideration, there

TABLE IX.

Line.	λ (referred to CuL_α = 13·306 Å.).	E (volts).	Appr. width of the lines.
Al K_β	7·952 } ±0·002 Å.	1552	
Al $K_{\alpha\,3,4}$ ...	8·262 } ±0·002 Å.	1494	
Al $K_{\alpha 1,2}$ ...	8·323 } ±0·002 Å.	1483	
Mg $K_{\alpha 3,4}$ ...	9·799 } ±0·003 Å.	1260	
Mg $K_{1,2}$ ...	9·874 } ±0·003 Å.	1250	
Na K_α	11·885 ±0·004 Å.	1038	
F K_α	18·275 ± 0·007 Å.	675·5	
O K_α	23·567 ± 0·02 Å.	523·8	
N K_α	31·557 ± 0·03 Å.	391·2	0·5 Å.
C K_α	44·54 ± 0·04 Å.	277·2	1 Å.
B K_α	67·71 ± 0·1 Å.	182·3	2 Å.
Be K_α	115·7 ± 0·15 Å.	106·7	10 Å.

would be no meaning in indicating the wave-lengths of the lightest elements with the accuracy obtained in this research. Instead Table IX. gives the range within which the wave-lengths might be indicated. The range is of the order of the interval between the maximum and the middle of the blackening.

I am greatly indebted to Professor Siegbahn, who suggested the research, and whose friendly encouragement and fruitful advice were essential to its successful completion. Mr. Ivar Lindell, instrument maker for the University, was responsible for the painstaking construction of the apparatus.

Upsala,
Physics Laboratory of the University,
June 1930.

LX. (i.) *The End-corrections of an Open Organ Flue-pipe; and* (ii.) *The Acoustical Conductance of Orifices.* *By* A. E. Bate, *M.Sc., Northern Polytechnic, London* *.

Abstract.

(i.) The end-correction at the mouth of an organ flue-pipe is shown to be independent of the frequency, but to depend on the dimensions of the mouth and on the sectional area of the pipe. The correction has the same value whether the pipe be open or closed, and is unaffected by the motion of the air-jet. It is shown that the correction α, in terms of A, the area of the pipe, and ω, the area of the mouth, may be represented by

$$\alpha = \frac{A}{k.2\sqrt{\omega/\pi}},$$

where k is a constant. This is of linear dimension, as is to be expected.

The correction β at the open end is found to be independent both of the dimensions of the mouth and of the frequency. It is somewhat larger than the usually accepted value, being given by

$$\beta = 0{\cdot}66\mathrm{R}.$$

R is the radius of the pipe.

(ii.) The conductance C of a circular orifice in the otherwise closed end of a cylindrical resonator is shown to be closely represented by the expression

$$\mathrm{C} = 2^{d/\mathrm{D}}.d,$$

d being the diameter of the orifice and D that of the pipe. This formula is also applicable to square orifices if d represents the diameter of a circle equal in area to the square. In a similar manner the conductance of a rectangular orifice may be determined when almost square, but for narrow rectangles the conductance must be treated as that of an ellipse of equal area, the ratio between the axes being the same as the ratio between the sides of the rectangle.

* Communicated by Dr. Reg. S. Clay.

Part I.

§ 1. In the two papers already published, the effect of wind-pressure and of the height of the mouth on the frequency of an organ pipe * and upon the end-correction at the mouth of a stopped pipe † have been dealt with. These will be referred to as the first and second papers respectively in this communication.

In the present paper it is shown that the results of the second paper are applicable to the mouth of an open pipe; the corrections at the open end are also included. In addition, the gap in the second paper between the results for frequencies of 128 and 256 has been bridged by including a frequency of 192 vibrations per second, which was obtained by comparison with a specially constructed fork.

The expression $\frac{V}{nh}=6{\cdot}17$ was established in the first paper as the relationship between V, the velocity of the air-jet; n, the frequency of the pipe; and h, the distance from the lip to the slit from which the air issues when the pipe is speaking its most stable note, the slit being 0·12 cm. wide. This relationship was used to determine the air-pressures required for the different heights of the mouth at the different frequencies.

§ 2. The apparatus described in the former papers has been again used for these further experiments. The pipe has a movable lip, which was adjusted so that the height of the mouth was 1·5 cm. The pipe was then blown with the pressure that has been found to be required to give a particular jet-frequency. The frequencies used were 132, 196, 260, 292, and 324; these were obtained by adjusting the length of the pipe to be approximately in tune with forks vibrating 128, 192, 256, 288, and 320 times per second respectively; the length was then decreased until there were four beats per second between the fork and the pipe, the beats being timed with a metronome. This method admits of very close adjustment, whereas true unison is very difficult to detect by ear.

The length of the pipe was obtained by placing a measuring rod inside the mouth and adjusting it so that the zero end coincided with the end of the pipe; an index sliding

* Phil. Mag. viii. p. 750 (Nov. 1929).
† Phil. Mag. ix. p. 23 (Jan. 1930).

on the rod was then brought into contact with the mouth and clamped to the rod; the position of this index thus indicated the length of the pipe. These measurements were taken both with the pipe open and closed at each frequency.

The whole procedure was then repeated with the height of the mouth altered to 1·25 cm., and again with it altered to 1·0 cm.

The difference between the lengths of the open pipe and of the corresponding closed pipe was taken as the length of the open pipe above the node, *i. e.*, the nodes in both cases were assumed to be at the same distance from the mouth. The amount by which the length above the node falls short of the quarter-wave-length is the open end-correction, and the amount by which the closed pipe falls short of the same quantity is the mouth end-correction.

§ 3. In § 9 of the second paper the end-corrections at the mouth for each height of the mouth were shown to remain practically constant when the length of the pipe is increased by one or by two half-wave-lengths. This also holds for the open pipe, so that the wave-lengths can be measured by lengthening the pipe until it recovers its initial frequency. One result will illustrate this, the frequency being 260 :—

	1st length.	2nd length.	Half-wave-length.
Closed pipe	25·1	90·0	64·9
Open pipe	55·8	120·6	64·8

The length of the half-wave calculated from the velocity of sound at this temperature is 65·0 cm.

Results.

§ 4. The actual readings obtained, and the resulting corrections, are set out in the following tables. The lengths of the pipe are all given in cm.

TABLE I.

Corrections when height of mouth = 1·5 cm.

Frequency	132	196	260	292	324
Closed pipe (i.).....	56·8	36·1	25·1	21·7	19·2
Open pipe	119·7	77·6	55·8	49·1	43·7
Closed pipe (ii.)	185·7	122·6	90·0	79·9	72·0
$\lambda/4$.....	64·45	43·25	32·45	29·1	26·4
Corrections. Open-end	1·55	1·75	1·75	1·7	1·8
Mouth	7·65	7·25	7·35	7·4	7·2
Total	9·2	9·0	9·1	9·1	9·0

TABLE II.

Corrections when height of mouth = 1·25 cm.

Frequency	132	196	260	292	320
Closed pipe (i.)	56·1	35·4	24·5	21·1	18·4
Open pipe	119·2	77·0	55·3	48·4	43·1
Closed pipe (ii.)	184·7	122·2	89·5	79·2	71·1
λ/4	64·3	43·4	32·5	29·05	26·35
Corrections. Open-end	1·2	1·8	1·7	1·75	1·65
Corrections. Mouth	8·2	8·0	8·0	7·95	7·95
Corrections. Total	9·4	9·8	9·7	9·7	9·6

TABLE III.

Corrections when height of mouth = 1·0 cm.

Frequency	132	196	260	292	320
Closed pipe (i.)	54·8	34·2	23·5	20·1	17·5
Open pipe	117·7	75·9	54·1	47·3	42·05
Closed pipe (ii.)	182·9	121·3	88·1	78·1	70·2
λ/4	64·05	43·55	32·3	29·0	26·35
Corrections. Open-end	1·15	1·9	1·7	1·8	1·8
Corrections. Mouth	9·25	9·35	8·8	8·9	8·85
Corrections. Total	10·4	11·2	10·5	10·7	10·65

These measurements were read to the nearest 0·5 mm., and are believed to be correct to within 1 mm. up to 100 cm.; hence the end-corrections should be accurate to within 2 mm. for all frequencies other than 132, and to within 4 mm. for that frequency. Discrepancies arise owing to changes in temperature; this accounts for the different values of the half-wave-lengths given above for a particular frequency, which were obtained at different times. To avoid errors due to this cause, the readings in any one series were taken as rapidly as possible. The poor agreement of the end-corrections for the lower frequencies in Tables II. and III. is probably due to the fact that the low pressures required were not far above the minimum values necessary to elicit notes of these frequencies.

§ 5. It has been assumed that the node in the open pipe occupies the same position as the closed end of the closed pipe when the pipe is giving the same note under identical conditions of blowing. This is not necessarily true, as the energy is being transmitted through the node for the maintenance of the vibrations in the upper portion, and to supply the energy that is being dissipated from its open or partially open end when the pipe is not closed.

Results, however, justify the assumption, for the difference between the lengths of the open pipe and of the corresponding closed pipe is the same at all intensities within the limits of experimental error ; hence the transmission of energy by the node does not cause a noticeable alteration in its position.

§ 6. *Discussion of Results.*

After an alteration has been made in the height of the mouth, the alteration in the length of the open pipe which is necessary in order to maintain a note of given frequency is seen from the above tables to be due to an alteration in the end-correction at the mouth ; it follows that the open-end correction is independent of the intensity of the note over the range of the pressure used, this intensity being governed by the jet-velocity. The pressure did not exceed 10 cm. of water. The results also prove that the open-end correction is independent of the height of the mouth and of the frequency. The mean value of the open-correction, omitting the doubtful values for the lowest frequency in Tables II. and III., is 1·74 cm. This is somewhat larger than the value of the end-correction of a resonance tube as determined by the usual tuning-fork method, which, for a tube of this diameter, would amount to 1·53 cm. Irons * draws attention to the fact that this method of obtaining the end-correction is untrustworthy, and quotes Boehm† : "A maximum of intensity outside the tube may not indicate that the resonator is nearest to unison with the pitch produced." In the present experiments forks are used as standards of comparison, and are, of course, independent of the exciting agent, the jet. Boehm gives the mean value of the end-correction as 0·656R. The corresponding figure obtained from the present results is 0·657R. The presence of a large flange increases this to about 0·84R (see § 12).

§ 7. On reference to the tables, it will be seen that the end-corrections at the mouth are, within reasonable limits, constant for each height of the mouth, and are independent of the frequency and (except for very low pressures) of the velocity of the air. The mean values of these corrections are 7·4, 8·0, and 9·0 cm. when the heights of the mouth are respectively 1·5, 1·25, and 1·0 cm. The

* Phil. Mag. v. p. 592 (Mar. 1928).
† Phys. Rev. xxxi. p 341 (1910).

diameters of circles that would have areas equal to the areas of the mouth when it has these heights are 2·70, 2·46, and 2·20 cm. respectively; these were called the "equivalent diameters" in the second paper, and are approximately equal to the conductance of the mouth in each case. In that paper the relationship between the end-corrections α and the conductances C was expressed by $C=\frac{A}{\alpha}$, in which A stands for the area of the cross-section of the pipe. This formula would give the three values of C as 2·98, 2·76, and 2·45 cm. respectively. The difference between these theoretical values and the practical results is partly attributable to the shape of the mouth, the formula being strictly applicable only when the mouth is a circular orifice. This point is further dealt with in Part II. (§ 16).

§ 8. The ratio between the conductances and the equivalent diameters is 1·1 nearly in all three cases, so that

$$\alpha=\frac{A}{C}=\frac{A}{1\cdot1\ (\text{equivalent diameter})}.$$

Since the equivalent diameter $=2\sqrt{\omega/\pi}$, where ω stands for the area of the mouth, the formula for the mouth-correction may be written generally

$$\alpha=\frac{A}{k\cdot2\sqrt{\omega/\pi}},$$

in which k is a numerical value depending on the shape and size of the mouth and on the presence of obstructions such as the "ears" which are usually fixed to each side of the mouth of an organ pipe, for these factors vary the conductance. For pipes in the same stop—an open diapason, for example—the value of k should be constant; in any case, it probably lies between 1·0 and 1·5, so that for such a set of similar pipes the mouth-correction is proportional to the sectional area of the pipe, and is inversely proportional to the square-root of the area of the mouth.

§ 9. An ordinary open cylindrical organ pipe of diameter 5·8 cm., designed to give 256 vibrations per second, was tuned at the correct wind pressure by means of the sleeve ("tuning top") fitted for that purpose. It was then found to measure 56·9 cm. from languid to open end. The half-wave-length at the temperature of the room was 66·3 cm.;

hence the total correction was equal to 9·4 cm. Allowing 1·9 cm. for the open end-correction, the mouth-correction was 7·5 cm. The dimensions of the mouth were : width, 4·45 cm. ; height, 1·8 cm. Substituting these values in the formula, we find that $k=1{\cdot}10$. The close agreement with the results obtained with the experimental pipe probably comes about because the presence of the ears in the ordinary organ pipe compensates for the unusual position of the mouth of the experimental pipe.

The open diapason pipe is usually made with a mouth of which the breadth is equal to one-quarter of the circumference, and the height to one-quarter of the diameter. Such a mouth will have an equivalent diameter equal to the radius of the pipe ; in this case the formula reduces to $\alpha=\frac{\pi}{k}.\mathrm{R}$. If k is taken as 1·1, this becomes 2·85R, so that the total correction is then about 3·5R.

In delicate stops (Dulciana, Gamba, etc.) the area of the mouth of a pipe varies from one-fifth to one-sixth of the sectional area of the pipe ; this increases the mouth-correction for such stops. On the other hand, the mouth of a pipe of a flute stop is usually made equal to about one-third of the area of the pipe, and in this case the mouth-correction is less.

(Organ builders usually make their open pipes about 3·3R short of the half-wave-length, and then trim them down as required ; final tuning is accomplished by means of the tuning-top.)

Part II.

§ 10. Lord Rayleigh* gave the conductance of an extremely short cylindrical pipe as with infinite flanges at the ends as

$$\frac{\pi\mathrm{R}^2}{\mathrm{L}+\frac{1}{2}\pi\mathrm{R}},$$

in which R is the radius and L the length of the pipe ; the second term in the denominator is the sum of the two end-corrections. He proceeds to show that if the two flanges approach until $\mathrm{L}=0$, the conductance becomes 2R ; *i. e.*, the conductance of a circular orifice in an infinite plane of negligible thickness is equal to the diameter.

* 'Sound,' ii. p. 181.

If, now, a cylinder whose dimensions are large compared with those of the orifice is supposed to be fixed to one side of the flange, with its axis concentric with the orifice, the conductance of the latter will remain practically unaltered. On decreasing the diameter of the cylinder (which is supposed closed at its unattached end), the conductance of the orifice alters, and eventually, when the diameters are equal, we have a pipe closed at one end and fitted with an infinite flange at the other. The correction at one end will now be eliminated, and the conductance becomes

$$\frac{\pi R^2}{\frac{1}{4}\pi R} = 4R,$$

i.e., the conductance of the open end of a pipe fitted with an infinite flange is equal to twice the diameter.

Thus the limiting values of the conductance of a concentric circular orifice on the end of a circular pipe are d and $2d$, d being the diameter of the orifice. A simple formula, which fits both extreme cases, is $C = 2^{d/D} \cdot d$, where D is the diameter of the pipe and C the conductance, for when $d=0$, $C=0$; and when $d=D$, $C=2D$ *.

Substituting this expression for the conductance in the equation $\alpha = \frac{A}{C}$, we get

$$\alpha = \frac{A}{2^{d/D} \cdot d}.$$

The truth of this formula for values between the two limiting values can be readily tested by the method employed in Part I. For this purpose nine caps were constructed to fit over the open end of the open pipe. In the centre of the plane-face of five of these caps circular holes were drilled, the diameters being 1, 2, 3, 4, and 5 cm. respectively. In the four remaining caps square holes were cut, the sides being 1, 2, 3, and 4 cm. long respectively.

Subsequently six additional caps were used, the apertures being rectangular and of dimensions (in cm.):

$$4\times3,\ 4\times2,\ 4\times1{\cdot}5,\ 4\times1,\ 3\times2,\ \text{and}\ 3\times1.$$

§ 11. The end-corrections were found for the capped end of the pipe with the five frequencies previously used, each of the caps being used in turn. The results obtained with

* [*Note.*—This limit is probably somewhat smaller than 2D, as $\frac{1}{4}\pi R$ is the lower limit of the end-correction of a flanged tube.]

the circular orifices are given in Table IV. The upper part of the table gives the difference between the lengths of the closed pipe and the complete pipe in each case, the lengths being measured from the inside of the caps. The wave-lengths were obtained by the method previously used. (Different values for a particular frequency were due, as before, to variation in temperature.)

The corrections are set out in the second part of the table ; they were obtained by subtracting the length above

TABLE IV.

End-corrections for circular orifices of various diameters.

Height of mouth		1·5	1·25	1·5	1·25	1·5	1·25	1·5	1·25	1·5
Frequency		132	196		260		292		324	
Length of pipe when diams. of orifices were	1 cm.	44·0	24·1	24·8	16·2	16·7	13·1	13·7	10·7	11·7
	2	54·9	34·1	34·1	24·0	24·1	20·5	20·7	17·4	18·1
	3	59·4	38·2	38·2	27·7	27·5	24·3	24·4	21·4	21·4
	4	61·4	40·05	40·0	29·5	29·5	26·0	26·1	23·3	23·2
	5	62·5	41·0	41·0	30·5	30·3	27·0	27·1	24·25	24·1
Open pipe	5·3	62·9	41·6	41·5	30·8	30·7	27·3	27·4	24·7	24·6
$\lambda/4$		64·45	43·4	43·25	32·5	33·45	29·05	29·1	26·35	26·3
Corrections for orifices of diams.	1 cm.	20·45	19·3	18·45	16·3	15·75	15·95	15·4	15·65	14·6
	2	9·55	9·3	9·15	8·5	8·35	8·55	8·4	8·95	8·2
	3	5·05	5·2	5·05	4·8	4·95	4·75	4·7	4·95	4·9
	4	3·05	3·35	3·25	3·0	2·95	3·05	3·0	3·05	3·1
	5	1·95	2·4	2·25	2·0	2·15	2·05	2·0	2·1	2·2
Open pipe	5·3	1·55	1·8	1·75	1·7	1·75	1·75	1·7	1·65	1·7

the node from the quarter-wave-length. Two heights of the mouth were used except for the first frequency (132), so that, in conformity with the formula $\frac{V}{nh}=6{\cdot}17$, two different values of V, the velocity of the air-jet, were necessary at each of the remaining frequencies. Any alteration in velocity is accompanied by an alteration in the intensity of the note produced, as stated in § 6.

It will be seen that the corrections for the larger orifices are independent of the wave-length and of the intensity, within reasonable limits. For the smaller orifices, however, the correction varies both with the frequency and with the intensity. The intensity variation may be due to the flow of air from the jet which travels through the pipe and

issues from the orifice ; at low pressures and with large orifices this flow has no appreciable effect on the correction. The variation with frequency may be due to the short length of the pipe that becomes necessary when the orifice is small, for then the diameter can no longer be neglected in comparison with the length. For this reason the values obtained with the lower frequencies and longer pipes should more nearly agree with the values obtained with the formula.

§ 12. The means of the above corrections are respectively : 1·7, 2·1, 3·2, 4·9, 8·8, and 16·9 cm. for orifices of diameter 5·3, 5·0, 4·0, 3·0, 2·0, and 1·0 cm. For such orifices in an infinite flange the calculated corrections would be 2·1, 2·3, 3·3, 5·0, 8·5, and 19·4 cm. A flange about 1 metre square was found to increase the corrections by 0·5, 0·5, 0·4, 0·4, 0·35, and 0·35 cm. respectively, *i. e.*, the pipe had to be shortened by these lengths to maintain the original frequencies when the flange was added. Thus the corrections with the flange become 2·2, 2·6, 3·6, 5·3, 9·15, and 17·25 cm.

These results are roughly 0·3 cm. larger than the calculated values ; this is to be accounted for by the fact that the thickness of the plate containing the orifice has been ignored, for the thickness reduces the conductance, and therefore increases the end-correction. The smaller discrepancy between the calculated and measured values of the open end-correction, amounting to 0·1 cm., where the thickness of the orifice does not arise, supports this view.

The end-corrections, with and without the flange, are shown in the graph (fig. 1). The curve gives the relationship between the diameters of the orifices and the corrections calculated from the proposed formula.

§ 13. The means of the experimental results obtained with square orifices are given in Table V. :—

Table V.

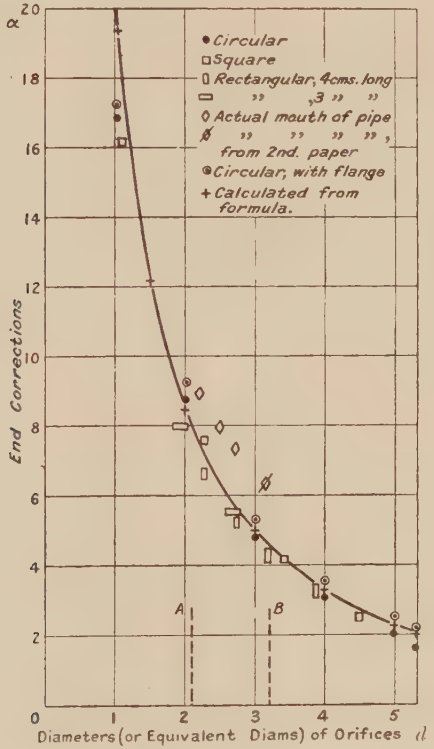
End-corrections with square orifices (unflanged).

Length of side of orifice in cm.	4	3	2	1
End-correction	2·6	4·2	7·6	16·2
Equivalent diameter.....	4·5	3·4	2·25	1·1

The relationship between the correction and the equivalent diameter is shown on the graph (fig. 1), from which it is seen that the correction for a square orifice is the same as that of a circular orifice of equal area.

§ 14. The end-corrections were next obtained with the rectangular apertures. The dimensions, equivalent dia-

Fig. 1.



meters, and mean values of the corrections are shown in the following table :—

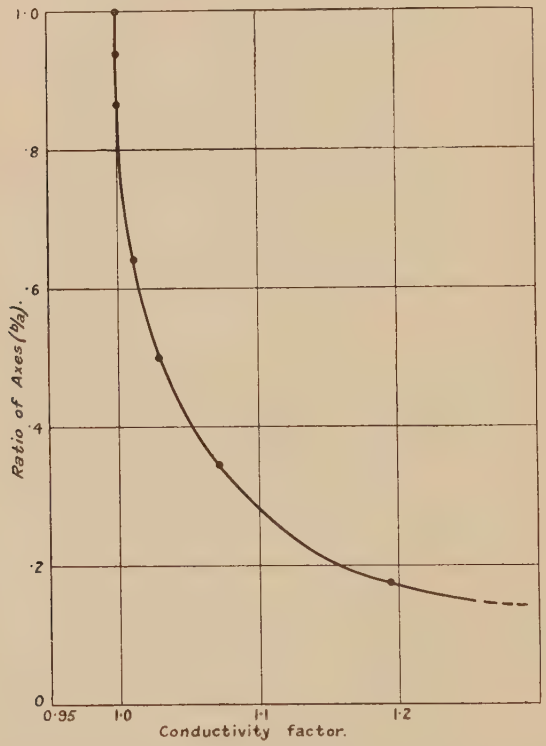
TABLE VI.

End-corrections with rectangular orifices (unflanged).

Dimensions in cm...	4×3	4×2	4×1·5	4×1	3×2	3×1
End-corrections ..	3·3	4·4	5·35	6·7	5·5	8·0
Equivalent diameters	3·9	3·2	2·75	2·25	2·75	1·95

The first four results, together with that for the square orifice of side 4 cm. (§ 13) resemble the end-corrections at a variable mouth of corresponding dimensions, and may be compared with the results recorded in Tables I., II., and III. On reference to the graph it will be seen that the first four results given in Table VI. deviate from the calculated curve as the ratio length/breadth is increased. The same applies to the orifices of length 3 cm. Thus the end-correction

Fig. 2.



for the orifice measuring 3×2 cm. is greater than that for the orifice measuring $4 \times 1{\cdot}5$ cm., although these have equal areas. It follows that the conductance of a rectangular orifice of constant area increases with increase in the ratio length/breadth.

§ 15. In this connexion it is interesting to recall that Rayleigh* has shown, from theoretical considerations, that

* 'Sound,' ii. p. 179.

the conductance of an elliptical orifice of a fixed area increases as the eccentricity is increased. He calculated the ratios of the conductivity of ellipses to those of circles of equal area, the ratio of the axes of the former varying from 0 to 1.

It appeared probable that the same factors would hold in the comparison of the conductivity of a rectangle with that of a square of equal area, when the ratio of the sides of the rectangle replaced those of the axes of the ellipse. To determine these factors of conductivity the results which Rayleigh had calculated were plotted in a graph (fig. 2), and the conductance factors for the ellipses whose axes are in the same ratio as the sides of the rectangular orifices were read off from the curve. These factors are entered in the second row of Table VII.

The end-corrections of the square orifices (unflanged) which would have apertures equal in area to the rectangular apertures used were next read from the graph (fig. 1). Since the end-corrections are inversely proportional to the conductances, the end-corrections thus found must be divided by the conductivity factors to obtain the true end-corrections. The results are shown in Table VII. :—

TABLE VII.

Calculated corrections for rectangular apertures.

Dimensions in cm...	4×3	4×2	4×1·5	4×1	3×2	3×1
Conductivity factors.	1·00	1·03	1·06	1·12	1·01	1·08
End-corrections for square orifices of equal areas.	3·4	4·4	5·6	7·6	5·5	8·8
Calculated end-corrections for rectangular orifices.	3·4	4·3	5·3	6·8	5·4	8·1
Actual corrections for rectangular orifices.	3·3	4·4	5·35	6·7	5·5	8·0

These readings are in excellent agreement with those given in Table VI., which are included above for comparison. It follows that, just as a square orifice has practically the same conductance as a circular orifice of equal area used under similar conditions, so a rectangular orifice has approximately the same conductance as an elliptical orifice of equal area, providing the ratio of the

axes of the ellipse is the same as the ratio of the sides of the rectangle.

These results extend Rayleigh's suggestion that any orifice may be treated as circular if it does not differ too much from a circle, to the case of a rectangle, which may be treated as an ellipse of equal area.

§ 16. Reverting to the question of the mouth correction which was discussed in Part I. (§ 7), the coefficient k in the equation $\alpha = \frac{A}{k.d}$ has been found to be practically constant. The ratios of the equivalent diameters of the openings of the mouth to the actual diameters of organ pipes range from 0·4 to 0·6 (Dulciana to Flute). This range is represented by that portion of the graph (fig. 1) between the ordinates marked A and B ; the curve in this region is nearly straight, and, since the end-correction for a rectangular orifice is smaller than that for a square one of equal area, the curve connecting the correction with the height of the mouth (the width remaining constant) will deviate from the calculated curve as the mouth decreases in height, and tend to become more nearly straight. This explains why k is practically constant. The mean values of k which were obtained with the experimental pipe are shown in the graph (fig. 1). They are above the curve, but this is probably due to the thickness of the lower lip, which forms a projection on the outside of the pipe and therefore decreases the conductance.

§ 17. The formula proposed for the conductance of an orifice fits the experimental results of two other experimenters. Richardson * obtained by measurement the lengths of a resonance tube when the open end of the latter was covered with caps containing circular apertures of various diameters. He then proceeded to calculate the lengths by means of the formula

$$\tan \frac{\pi L}{\lambda/2} = \frac{\lambda}{2\pi} \cdot \frac{C}{A},$$

C being the conductance of the orifice, which he assumed to be equal to the diameter, and A the sectional area of the tube. The other terms have their usual meanings. The tube was 4·3 cm. in diameter, and the frequencies

* Proc. Phys. Soc. xl. p. 206 (1928).

ranged from 1000 to 224 v.p.s. The calculated and actual lengths were plotted on the same graph, from which he concluded that "... the theoretical and experimental curves are similar, but that there is lack of agreement when r (radius of orifice) is large. This, one may judge, is due to a change in the dependence of C upon r. It is evident that some such change must take place as resonator conditions are approached. ..."

Repetition with a tube 2·2 cm. in diameter resulted in similar curves.

The writer repeated Richardson's calculations with the conductances obtained from the expression $C = 2^{d/D} . d$, and these gave much closer agreement with the measured values. (Allowance must be made for the absence of infinite flange, and also for the fact that resonance was obtained by holding tuning-forks over the orifices).

Again, Irons *, by fitting similar caps over the end of a Kundt's tube 4·7 cm. in diameter, found experimentally that the products of the conductances and the corresponding end-corrections, $C . \alpha$, were roughly 14·3 cm. when orifices of from 1 to 2 cm. diameter were used; the capped end was fitted with a large flange. The product of the diameters of the orifices and the corresponding end-corrections he found to be 11·0 cm.; so "... to reconcile theory with practice, the conductances of the orifices in question must be assumed to be somewhat larger than their diameters. ..."

From these values the approximate ratio of $\frac{C}{d}$ equals 1·3; if, however, we substitute 4·7 for D, and 1·0 and 2·0 for d in each case in the formula, the values of $\frac{C}{d}$ become 1·16 and 1·34 respectively.

Conclusions.

§ 18. The end-correction at the mouth of an organ flue-pipe has the same value whether the pipe be open or stopped, and may be obtained from the formula

$$\alpha = \frac{A}{k . 2\sqrt{\omega/\pi}},$$

* Phil. Mag. vii. p. 873 (May 1929).

in which A stands for the sectional area of the pipe, ω for the area of the mouth, and α the correction at the mouth-end of the pipe; k is a numerical coefficient, and is constant for a particular type of pipe.

The end-correction β at the open end of an unstopped pipe is shown to be represented by the expression $\beta = 0{\cdot}66\mathrm{R}$. This is higher than the usually accepted value.

Both end-corrections are, within experimental limits, independent of the intensity of the note and of the frequency. For low pressures the results are unreliable.

The conductance C of a circular orifice in an infinite flange at the end of a cylindrical pipe is closely represented by

$$\mathrm{C} = 2^{d/\mathrm{D}} . d,$$

in which d is the diameter of the orifice and D that of the pipe. This is approximately true for unflanged orifices, particularly when the orifices are small. When the orifice is square, or nearly so, the formula will give very close results if the aperture is regarded as circular and of the same area. For a rectangular orifice, as the ratio length/breadth is increased, the conductance increases beyond the value given in the formula. However, the factor which Rayleigh calculated to be the ratio between the conductivity of an elliptical aperture to that of a circular aperture of equal area is shown, experimentally, to be the same as the ratio between the conductivity of a rectangular aperture and that of a square aperture of equal area, provided the ratio of the axes of the ellipse is the same as the ratio of the sides of the rectangle.

This extends Rayleigh's suggestion that any orifice may be treated as circular if it does not differ too much from a circle, to the case of the rectangle which may similarly be treated as an ellipse of equal area.

The author wishes to acknowledge his indebtedness to Dr. R. S. Clay for much helpful criticism during the course of this work.

Whitsun, 1930.

LXI. *The Expansion of Metals at High Temperatures.* *By* Fdk. L. Uffelmann, *B.Sc., East London College* *.

Abstract.

An optical interference method, for measurements in three perpendicular directions on the same specimen, and for use up to 800° C., is described. The use of continuous temperature variation is made possible by a device for equalizing the temperature-lag of the platinum resistance thermometer and the specimen. Observations were taken during both heating and cooling of the specimen.

Results are given for tin, cadmium, zinc, lead, aluminium, copper, brass, cobalt, nickel, and steel, and, where possible, the quadratic and Thiesen's relations are fitted. Tin, cadmium, and zinc show pronounced anisotropic properties; while for cobalt, nickel, and steel the coefficient of expansion curve during heating is different from that during cooling, cobalt showing a sharp peak at 450° C. on heating and at 330° C. on cooling.

THIS work was undertaken at the suggestion of Professor C. H. Lees to provide more reliable information on the expansion of the metals tin, cadmium, zinc, lead, aluminium, copper, brass, cobalt, nickel, and steel from air temperature up to 700° C. A modified Fizeau method was used, as it requires a small specimen only to be kept at uniform temperature, and is sufficiently sensitive. The apparatus in its early form was designed by Mr. Madge, B.Sc., in consultation with Prof. Lees.

The specimens were cubes of side 4 mm. Expansion measurements were made in three perpendicular directions on the specimen, and the cubical expansion of the specimen was deduced.

The length of the specimen was found with a standard screw gauge, and could be estimated to 0·0001 cm. or to 1/4000 of the length of the cube.

The passage of a fringe could be estimated to from 1/20–1/40 fringe. This, over a range of 20–40 fringes, gives an error to the expansion coefficient varying from 1/400–1/1600.

* Communicated by Prof. C. H. Lees, F.R.S.

In the earlier experiments the temperature was measured by means of a platinum wire wound round a silica core, in a silica tube of about 4 mm. diameter, with its axis at the same level as the specimen. This method was found not to give the temperature of the specimen with sufficient accuracy. In the later form used in the following work a winding of asbestos string replaced the silica tube, and the whole was inserted in a block of brass of mass so determined that the lag of temperature of the brass and the metal specimen should be the same.

The error of measurement of the temperature interval was of the order of 1/40 degree Centigrade. This, over the average temperature interval of 40 to 60 degrees, results in an error of 1/1600 to 1/2400 to the expansion coefficient.

The maximum total error to the expansion coefficient varies from $1/400+1/1600+1/4000=0{\cdot}003$, or ·3 per cent., to $1/1600+1/2400+1/4000=0{\cdot}001$, or 0·1 per cent. This means that in the majority of cases there is doubt over the fourth significant figure of the expansion coefficient.

The Apparatus.

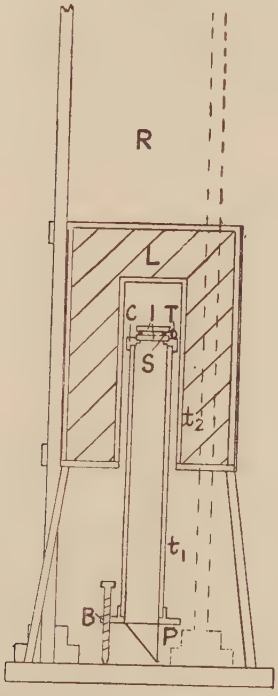
The Interference Plates.—The apparatus consists essentially of two fused quartz interference plates (I, fig. 1) $2\frac{1}{2}$ cm. in diameter, separated by the specimen under test. In the early experiments the specimen was placed on the middle of the lower plate and formed the sole support of the upper interference plate, the interference pattern being visible around the specimen. Later, however, two supplementary supports of the same material and of equal length were introduced to reduce tilting of the upper plate, caused by non-uniform extension of the specimen. The lower surface of the upper interference plate is lightly platinized, while the lower interference plate is uncoated *. The interference plates are ground with their two surfaces making an angle of about 7 minutes, just sufficient to prevent confusion of the fringes used in the measurements. The lower interference plate is supported at the top of a

* Theoretically the best fringes are obtained when the upper plate is heavily coated while the lower plate is lightly coated. A palladium surface on the upper interference plate was found to be not durable at high temperatures. Messrs. Hilger undertook to coat the plate with platinum by the "liquid" process. The limit of durability of this coating was stated to be 800° C.

silica tube (t_1), 4 cm. diameter, by a Steatite cap (C) cemented to the tube. The lower end of the silica tube is cemented into a brass holder (B) standing upon three massive brass screws and supporting a 45 degree prism (P).

The Furnace.—The heating is performed by an electric furnace having an inner tube of silica (t_2), which gives from 2–3 mm. clearance when lowered over the tube (t_1). To reduce convection currents this tube is only open at the

Fig. 1.



bottom. It is wound with two heating coils—one uniformly along the whole length, the second a small coil at its lower end to make up for loss of heat at the mouth of the furnace.

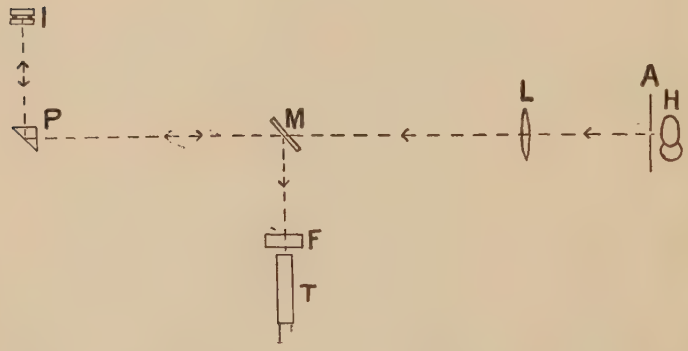
The outside of the furnace is of compressed asbestos sheet bound with steel right-angle strips. The space between the silica tube and the outside walls is packed with asbestos wool (L). The lagging was so good that, even when the furnace had an interior temperature of 800° C. or more,

the outside of the furnace was only in the neighbourhood of 50° C.

To admit of adjustment of the interference plates the furnace slides vertically upwards on three steel bars (R), rigidly connected together at the top, and screwed firmly to a base-board, which is in turn screwed to the bench.

The Optical System (see fig. 2).—Light from a mercury-vapour lamp (H) passes through a hole in a screen, illuminates an adjustable aperture (A), is rendered parallel by a lens (L), and passes through the semi-silvered piece of plane glass (M) to the 45 degree prism (P) at the bottom of the tube t_1, and up the tube to the interference plates (I). The reflected light returns down the silica tube through the

Fig. 2.



prism, and is reflected by the semi-silvered plate into the mercury green filter (F) and the telescope (T). The aperture, the lens, the reflecting mirror, the filter, and the telescope were all clamped firmly to substantial stands screwed to the benches.

For stability the whole apparatus was set up in the basement, and to reduce vibration the bench supporting the interference apparatus was mounted on rubber blocks.

The Thermometer.—The thermometer was of gauge 40 platinum wire, having a resistance of about 1 ohm at air temperatures. In the early experiments the platinum wire was welded to a pair of 22 gauge copper leads. To act as a compensator a short piece of 40 gauge platinum wire was welded between the ends of another pair of copper leads. The copper leads, however, deteriorated rapidly,

and it was found necessary to insert lengths of 22 gauge platinum wire to extend about 5 cm. out of the furnace, where they were silver-soldered to the copper leads. The leads were kept in position by passing through four holes in small pieces of slate, and at intervals were bound to the silica tube with pieces of nickel wire, insulated from the platinum with mica. The resistance of the thermometer was measured with a Callendar and Griffiths bridge made by the Cambridge Instrument Co.

The Adjustment of the Apparatus.

The three specimens are placed in position on the lower interference plate, and the cover plate is lowered gently on to them. If the specimens have been accurately ground, the reflected images of the aperture (A) from the facing surfaces of the two interference plates, as seen in the telescope (T, fig. 2), will almost coincide. The lengths of the specimens are adjusted, by lightly rubbing on the finest emery paper, until a definite degree of overlap of the images is obtained which is known by experience to correspond, on re-focussing, to fringes of the most convenient width. The aperture (A) is then adjusted to give the correct degree of illumination for the production of distinct fringes.

Before observations are commenced the light beam is made a parallel one and normal to the plates.

Methods of Observation.

The furnace currents are adjusted so that one fringe passes about every 20 seconds at the steepest part of the heating curve.

The time of passage of every fringe is noted to the nearest second. In between the passage of consecutive fringes the Callendar and Griffiths bridge is balanced, and the time of balance is noted correct to the nearest second.

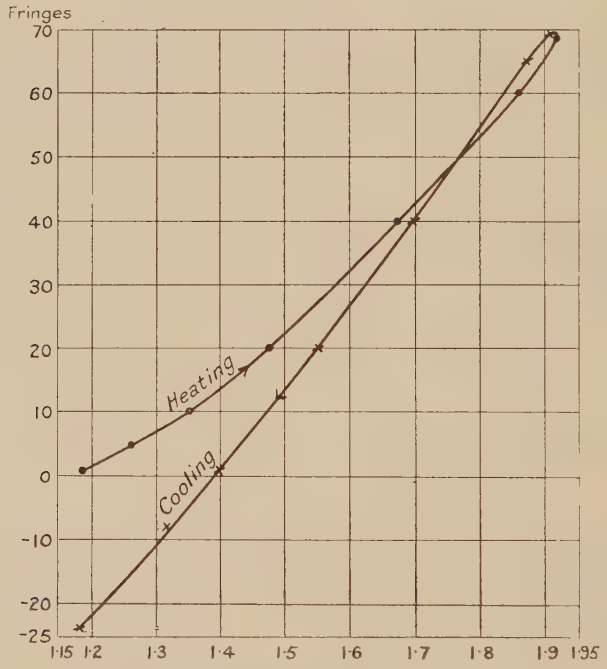
The resistances are adjusted periodically to keep the heating currents constant, and in experiments taken above 300° C. the currents are increased during the experiment. Just before the proposed maximum temperature for an experiment is reached the heating currents are reduced or cut off. Observations are continued, great care being taken not to miscount the fringes at the point where the cooling of the furnace commences. The experiment is

continued down to a temperature of 30–60° C., where the fringes pass at the rate of one every 5–10 minutes. A complete experiment takes from 4–7 hours.

Errors and Corrections.

Stress.—Before the experiment was performed the furnace, containing the specimens in adjustment, was heated to a temperature slightly greater than it was proposed to

Fig. 3.



Resistance of thermometer in ohms.

Results with badly annealed specimen of tin.

reach during the experiment, and then was allowed to cool slowly to relieve any stress in the specimens. In some cases a single heating was not sufficient. The graph (fig. 3) shows the results obtained with a specimen of tin after two previous heatings. It will be noticed that the rate of extension and the rate of contraction have entirely different values, but in the later heatings the two curves almost coincide.

Oxidation of Specimen.—In most cases this preliminary heating forms a skin of oxide round the specimen which, provided the specimen is not subsequently heated to an unduly high temperature, prevents further oxidation. In addition, the brass cubes were lightly nickel-plated and the copper cubes lightly gold-plated.

Error of Lag.—When the temperature of the furnace is changing the temperature of the specimen lags behind that of the thermometer, and on plotting the number of fringes passed against the temperature, the curve for heating does not coincide with that for cooling. This difference could also be produced by (1) relief of stress during the experiment, (2) oxidation of the specimen during the experiment, (3) a difference between the expansion and contraction coefficient (this was found for cobalt and nickel).

(1) and (2) can be overcome as explained above, while (3) is very pronounced when it occurs, and not easily confused with lag separation.

To prove in the case of a specimen of well annealed tin that (1) and (2) had been overcome observations were taken down to air temperature by gently lifting the furnace from over the specimens when the rate of cooling got unduly slow. It was found the specimen had the same length as at the start (see fig. 4).

It should be noted here that the distance between the curves for heating and cooling increased considerably when the furnace was lifted from the specimen, proving that the lag depends upon the rate of change of temperature (see fig. 4).

Reduction of Lag.—The introduction of a heavy copper cover * to enclose the specimen, interference plates, and thermometer failed to reduce the lag.

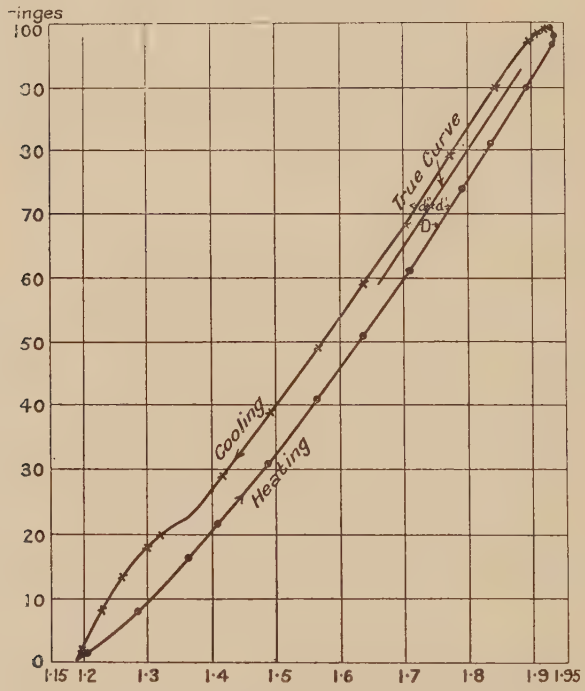
A piece of brass, having a water equivalent equal to the excess water equivalent of the two interference plates over that of the thermometer, was made to fit over the thermometer. The distance (D) (fig. 4) gives the sum of the deviations of the thermometer from the temperature of the specimen upon heating (d'), and upon cooling (d''), and was noted at a definite temperature in experiments taken over about 20 fringes, (1) without, and (2) with the piece of brass in position ((2) was found to reverse the lag). Then

* See W. Gray, Bull. Bur. Stand. p. 450 (1914-15).

a piece of brass was cut off, and the value of (D) again found, and the process repeated.

A graph was plotted with the weights of the "compensator" as abscissa, and the values of D as ordinate. The intersection of the curve with the abscissa gives the weight of the "compensator" when D is zero. The "compensator" was reduced to this weight, and upon trial it was

Fig. 4.



Resistance of thermometer in ohms.

Extension curve obtained without "Lag Compensator."

found that the lag was now very small; the improvement is illustrated by the two curves for tin (figs. 4 & 5).

A fresh "compensator" was needed for every material tested.

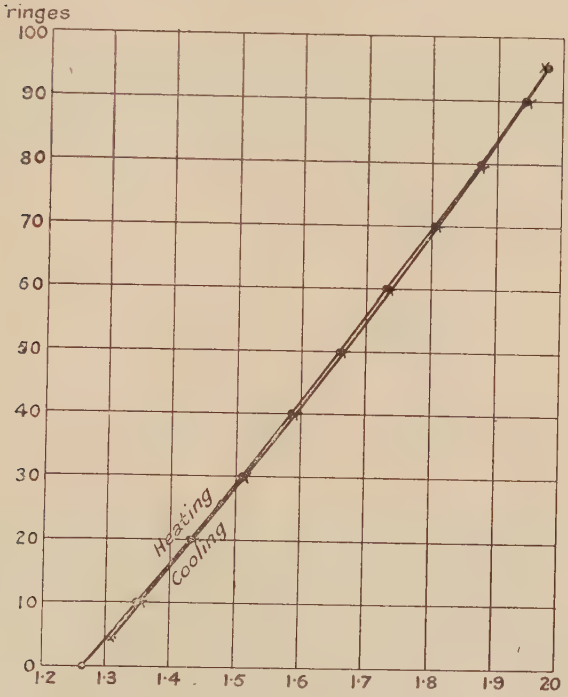
Correction for Lag.—The remaining lag was corrected for by taking it proportional to the rate of heating $\frac{dv}{dt}$.

During heating

$$v_1 = v_0 + b\frac{dv_0}{dt}, \quad \ldots\ldots\ldots \quad (1)$$

where v_1 is the temperature of the specimen, v_0 is the temperature registered by the thermometer, and b is a constant.

Fig. 5.



Resistance of thermometer in ohms.

Extension curve obtained with "Lag Compensators."

During cooling

$$v_1 = v_0' + b\frac{dv_0'}{dt}. \quad \ldots\ldots\ldots \quad (2)$$

Hence

$$v_0 + b\frac{dv_0}{dt} = v_0' + b\frac{dv_0'}{dt},$$

and

$$v_1 = v_0 - (v_0 - v_0') \frac{\frac{dv_0}{dt}}{\frac{dv_0}{dt} - \frac{dv_0'}{dt}}, \quad . \quad . \quad . \quad (3)$$

$$v_1 = v_0' - (v_0 - v_0') \frac{\frac{dv_0'}{dt}}{\frac{dv_0}{dt} - \frac{dv_0'}{dt}}. \quad . \quad . \quad . \quad (4)$$

The two expressions (3) and (4) give the true temperature of the specimen for any particular fringe, in terms of the temperature recorded at the passage of this fringe upon heating and upon cooling, and of the rates of heating and cooling.

No error is introduced, and a great deal of labour is saved if the formula

$$r_1 = r_0' - (r_0 - r_0') \frac{\frac{dr_0'}{dt}}{\frac{dr_0}{dt} - \frac{dr_0'}{dt}} \quad . \quad . \quad . \quad (6)$$

is used in place of (4). r is the resistance corresponding to the temperature v.

The Error Introduced by the Use of Three Supports.—The two auxiliary specimens were made in the shape of cubes of 4 mm. side, with the top cut away to leave a square of 2 mm. side, and both were cut, together with the actual specimen, in the same direction from the same block of material, so that they should expand equally.

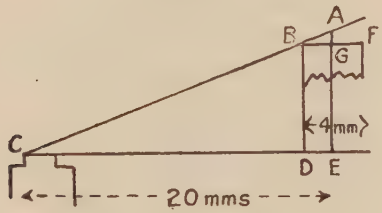
The two auxiliary supports were put in line at one end of the interference plate, while the actual specimen was placed as accurately as possible on the perpendicular bisector of the line joining the two supports, in a position very close to the thermometer.

When all three specimens were arranged in the same relative positions, it was found on heating that very little tilt of the plate occurred. If the actual specimen expands differently from the auxiliary supports, the plate will tilt. No error is introduced by this tilt provided the cross-wires of the telescope are focussed in the line of contact of the specimen with the interference plate (see fig. 6). The line

of contact is through B or F, and is parallel to the line joining the two auxiliary specimens. Suppose they are focussed midway along the length of the specimen at the point A. The perpendicular distance of the centre of the specimen from the supports (C) is about 20 mm. The error is represented by the length $AG - AE \cdot \frac{BG}{CE} = \frac{AE}{10}$. If AG is required in terms of fringes, then AE represents the excess number of fringes passed at A over the number which have passed at C.

It is only in the case of tin, cadmium, and zinc that any appreciable tilting of the interference plate was noticed. In the case of zinc the error was eliminated by cutting away the specimen to leave knife-edges on three perpendicular sides. The specimen was arranged so that the knife-

Fig. 6.



edge in use was parallel to the line joining the two support specimens. The cross-wires were focussed in the line of the knife-edge at a point just beside the specimen.

Correction for the Change in the Refractive Index of Air with Variation of Temperature and Pressure.—The number of fringes passed on heating from $T_1{}^0A$ to $T_2{}^0A$ is given by

$$N = \frac{2}{\lambda}[\mu_2(L+\Delta L) - \mu_1 L],$$

where λ is the wave-length of the light, μ_1, μ_2 are the refractive indices of air for the wave-length λ at the temperatures T_1, T_2 and the pressures p_1 and p_2 respectively, L is the length and ΔL the increase in length of the specimen. Assuming the pressure is constant during the experiment, and that $\frac{\mu - 1}{\rho}$ is constant, we get

to an accuracy of 0·001 per cent. that

$$\frac{1}{L}\cdot\frac{\Delta L}{\Delta T}=\frac{1}{L}\cdot\frac{N.\lambda}{2.\Delta T}+(\mu_0-1)\cdot\frac{273}{760}\cdot\frac{p}{T_1.T_2},$$

where μ_0 is the index at N.T.P., *i.e.*,

$$\alpha\ (\text{corrected})=\alpha\ (\text{uncorrected})+(\mu_0-1)\cdot\frac{273}{760}\cdot\frac{p}{T_1.T_2}.$$

For the mercury green line μ_0 has the value 1·0002933 *. Hence the correction is

$$0{\cdot}0001052\ .\frac{p}{T_1.T_2}.$$

This is required to one significant figure only, and is easily applied with the aid of a graph, in which the correction for equal temperature intervals is plotted against the mean temperature of the interval.

The Calibration of the Thermometer.

In all, four different thermometers were calibrated. The fixed points used for the calibration were

(1) The melting point of ice.
(2) The boiling point of water.
(3) The freezing point of tin..... 231·8(5)° C.
(4) The freezing point of cadmium ..... 320·9° C.
(5) The freezing point of zinc ..... 419·4(5)° C.
(6) The freezing point of NaCl ..... 801° C.

The Calibration at the Melting Point of Ice and at the Boiling Point of Water.—The usual type of apparatus was used for these determinations. In both cases the thermometer was enclosed in a long glass tube with the mouth plugged with asbestos wool.

The Calibration at the Freezing Points of the Metals.—The apparatus used is shown in fig. 7. It consists of a small electric furnace (F) with a central opening just large enough to hold a hard glass boiling tube (B). The furnace is supported vertically by a retort stand (R).

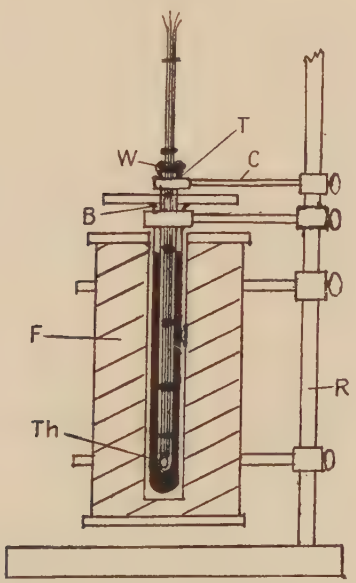
The thermometer (Th) was enclosed in a long hard glass tube (T) plugged with asbestos wool (W). The joints

* See Landolt u. Börnstein.

between the platinum and copper leads were screened from the furnace to avoid the production of varying e.m.fs. by unsteady heating.

After melting the calibration metal in the tube (B), the tube (T) was forced down into it and held in position by the clamp (C). The furnace was allowed to cool slowly, and resistance-time observations were made so as to obtain a freezing point curve.

Fig. 7.



Apparatus for thermometer calibration.

Calibration at the Freezing Point of NaCl.—The thermometer was enclosed in a silica tube about 15 cm. long, while the salt was placed in a tall fireclay crucible cemented into a muffle furnace.

Calculation of Thermometer Constants.—For a platinum resistance thermometer

$$r = r_0(1 + \alpha v + \beta v^2),$$

where r is the resistance of the thermometer at the temperature $v°$ C., and r_0 is the resistance at 0° C. α and β are the

required constants, and were calculated, by the method of least squares, from the calibration values of r and the corresponding values of v.

The temperature in terms of the thermometer resistance is given by

$$v = -\frac{\alpha}{2\beta} - \sqrt{\frac{1}{r_0\beta}} \cdot \sqrt{\frac{\alpha^2 r_0}{4\beta} + (r - r_0)}.$$

An example of a thermometer calibration is given below :—

Calibration Points.	Temperature v.	Resistance r.
(1) The melting point of ice.....	0 °C.	1·1275 ohms.
(2) The boiling point of water at 77·41 cm. pressure	100·51° C.	1·5146 ,,
(3) The freezing point of tin	231·85° C.	1·9968 ,,
(4) The freezing point of cadmium ...	320·9° C.	2·3154 ,,
(5) The freezing point of zinc	419·45° C.	2·6612
(6) The freezing point of NaCl	801° C.	3·8524 ,,

This gives

$$\alpha = 0{\cdot}0034696 \; ; \quad \beta = -0{\cdot}000\,000\,56391 \; ;$$

and

$$v = 3076{\cdot}37 - 1254{\cdot}1\sqrt{7{\cdot}1448 - r}.$$

The Calculation of Results.

The resistance of the thermometer at the time of passage of a fringe is first found by interpolation at intervals of 10–20 fringes. A curve is then plotted with the resistance of the thermometer as abscissa and the number of fringes passed as ordinate. Any necessary correction for lag is applied, and the temperature calculated. The expansion coefficients are then worked out, usually over ranges of 10–40 fringes, but when changes in the coefficient are rapid over smaller ranges. Finally, the correction for the change of refractive index of air with temperature is applied.

The final values for the three linear coefficients α_1, α_2, α_3, are plotted against the mean temperature. Wherever any systematic difference in α_1, α_2, α_3 occurs, the cubical coefficient (α_c) curve is plotted from the α_1, α_2, α_3 curves ; otherwise the mean linear coefficient (α_l) curve is plotted.

Calculation of the Constants A *and* B *in the relation*

$$V = V_0(1 + Av + Bv^2),$$

where V is the volume at the temperature v, and V_0 is the volume at 0° C.

If the points plotted for the cubical expansion coefficient fall on a straight line, then the relation holds good, and A is the intercept on the axis of α_c, while B is half the slope of the straight line.

Similarly the constants A_l, B_l, in the relation

$$L = L_0(1 + A_l v + B_l v^2)$$

are determined from straight line α_l curves.

Calculation of the Constants in Thiesen's Formula

$$\frac{dV}{dT} = K \cdot T^{n*}.$$

T is the absolute temperature,

V is the volume,

K and n are constants.

We may write the formula

$$\alpha_c = \frac{K}{V} \cdot T^n, \text{ or for unit volume } \alpha_c = KT^n.$$

If this formula holds, on plotting log α_c against log T we should get a straight line graph, whose intercept with the (log α_c) axis is log K, and whose slope is n.

The Constants of the Relation $\frac{dL}{dT} = K_l T^n$.

L is the length of the specimen.

For unit length the constant n has the same value as in the relation $\frac{dV}{dT} = K \cdot T^n$, while $K_l = K/3$.

The Results.

Tin.

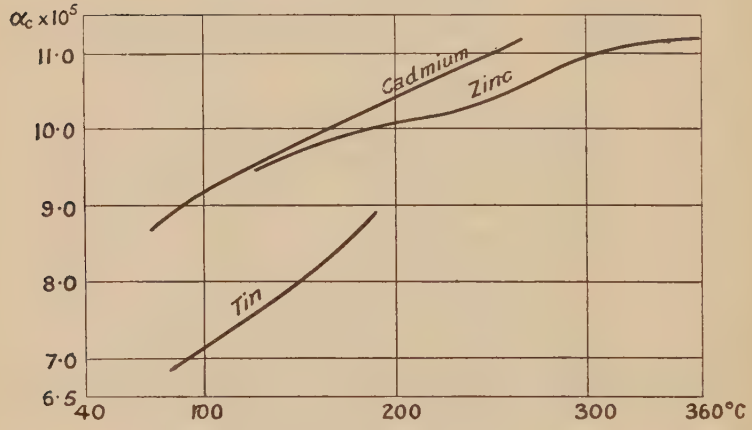
The linear coefficient of expansion for side 1 of the cube (α_1) was found to be much greater than the coefficients for the other two sides (α_2, α_3), *e. g.*, at 120° C. $\alpha_1 = 3{\cdot}38 \times 10^{-5}$, $\alpha_2 = 1{\cdot}92 \times 10^{-5}$, $\alpha_3 = 2{\cdot}18 \times 10^{-5}$. This seems to indicate that the axis of the crystal lies approximately perpendicular to the face side 1.

* See *Deuts. Phys. Ges. Verh.* x. pp. 410-415 (1908).

The values for the cubical coefficient are given below (see fig. 8).

Temperature v.	α_c.
80° C.	6·84(7) . 10^{-5}.
100° C.	7·14(5) ,,
120° C.	7·47(2) ,,
140° C.	7·82(6) ,,
160° C.	8·21(4) ,,
180° C.	8·65(5) ,,
190° C.	8·90(5) ,,

Fig. 8.



Cubical coefficients for Sn, Cd, and Zn.

Neither the Quadratic nor Thiesen's relation seems to fit the results, since both plots α_c against v, and log α_c against log v, have a definite curvature upwards. For the region 120–190° C. the mean values for the Quadratic constants are

$$A = 5{\cdot}05 \,.\, 10^{-5} \quad \text{and} \quad B = 9{\cdot}9 \,.\, 10^{-8}.$$

Cadmium.

The three linear coefficients were found different at air temperatures (*e.g.*, at 60° C. $\alpha_1 = 2{\cdot}37 \,.\, 10^{-5}$, $\alpha_2 = 2{\cdot}54 \,.\, 10^{-5}$, $\alpha_3 = 3{\cdot}50 \,.\, 10^{-5}$), but to approach each other towards the melting point of the metal.

The final values for the cubical expansion coefficient are as follows (see fig. 8) :—

Temperature v.	α_l.
70° C.	8·62(1) . 10^{-5}.
80° C.	8·81(4) ,,
90° C.	8·98(3) ,,
100° C.	9·14(3) ,,
110° C.	9·30(0) ,,
120° C.	9·44(3) ,,
130° C.	9·58(5) ,,
140° C.	9·71(4) ,,
150° C.	9·84(4) ,,
170° C.	10·07(3) ,,
190° C.	10·29(7) ,,
210° C.	10·52(7) ,,
230° C.	10·76(2) ,,
250° C.	10·99(1) ,,
268° C.	11·21(8) ,,

Thiesen's Constants.—The logarithmic plot gives two sets of constants :—

(1) 90–130° C..... $n=0{\cdot}626$; $K=2{\cdot}25 . 10^{-6}$.

(2) 130–270° C..... $n=0{\cdot}519$; $K=4{\cdot}27 . 10^{-6}$.

Constants of the Quadratic Relation.—This relation holds for the range 130–270° C. The constants have the value

$$A=8{\cdot}04(8) . 10^{-5} ; \quad B=5{\cdot}9 . 10^{-8}.$$

Zinc.

The three linear coefficients were found to be very different, *e. g.*, at 200° C. $\alpha_1=4{\cdot}12 . 10^{-5}$, $\alpha_2=3{\cdot}67 . 10^{-5}$, $\alpha_3=2{\cdot}29 . 10^{-5}$.

The values found for the cubical expansion coefficient are :—

Temperature v.	α_c.
120° C.	9·40(1) . 10^{-5}.
140° C.	9·59(9) ,,
160° C.	9·78(1)
180° C.	9·95(8) ,,
190° C.	10·03(5) ,,
200° C.	10·10(2) ,,
220° C.	10·20(0) ,,
240° C.	10·30(6) ,,
260° C.	10·51(3) ,,
280° C.	10·75(1) ,,
300° C.	10·94(8) ,,
320° C.	11·09(7) ,,
340° C.	11·17(2) ,,
360° C.	11·18(7) ,,

Above 180° C. the results are irregular (see fig. 8).

Thiesen's Constants.—The logarithmic plot gives a straight line for the region 120–180° C., which, when produced, meets the curve again as a tangent over the region 300–320° C. From this straight line we get :—

$$n = 0{\cdot}402\ ;\ K = 8{\cdot}54\,.\,10^{-6}.$$

The Constants of the Quadratic Relation.—The mean values for the range 120–360° C. are :—

$$A = 8{\cdot}50\,.\,10^{-5}\ ;\ B = 3{\cdot}9\,.\,10^{-8}.$$

Allotropic changes in zinc have been found by E. Cohen to occur at 64·9° C., 170° C., and 310° C.*. The decided change in the slope of the coefficient of expansion curve over the range 300–360° C. may correspond to the upper transition point. Similarly the change in the slope over the range 180–240° C. may correspond to the allotropic change which has been found at 170° C.

Lead.

The results given below are the mean linear coefficients (see fig. 9).

Temperature v.	α_l.
80° C.	2·89(6) . 10^{-5}.
100° C.	2·91(2) ,,
120° C.	2·95(0) ,,
140° C.	2·99(2) ,,
160° C.	3·02(1) ,,
170° C.	3·03(4) ,,
180° C.	3·05(9) ,,
190° C.	3·09(1) ,,
200° C.	3·12(1) ,,
220° C.	3·16(2) ,,
240° C.	3·20(0) ,,
250° C.	3·23(7) ,,
260° C.	3·30(2) ,,
280° C.	3·43(3) ,,

These results for lead divide themselves into four different sections :—(1) below 95° C. ; (2) from 95–170° C. ; (3) from 170–245° C. ; (4) from 245–280° C. An allotropic change occurs in lead at 50° C. according to

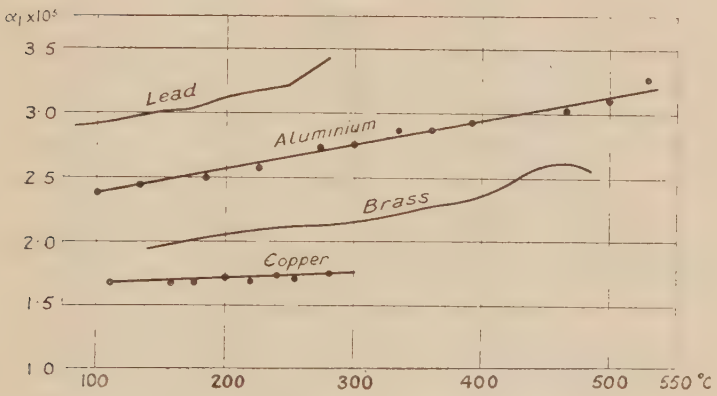
* See Mellor, 'A Treatise on Inorganic Chemistry,' iv. p. 430.

E.Cohen and W. D. Helderman, and at 59–62° C. according to E. Jänecke* ; the change in the slope of the expansion coefficient curve in the region of 95° C. may correspond to this transition point. No allotropic changes have been found which would explain the changes in the slope of the curve at 170° C. and 245° C.

Thiesen's Constants.—If we neglect the depression from 150–190° C., the logarithmic plot falls into two straight lines, which give :—

(1) 100–240° C. ..... $n=0{\cdot}306$; $K_l=4{\cdot}74 \,.\, 10^{-6}$.
(2) 250–280° C. ..... $n=1{\cdot}054$; $K_l=4{\cdot}44 \,.\, 10^{-8}$.

Fig 9.



Linear coefficients for Pb, Al, brass, and Cu.

The Constants of the Quadratic Relation.—Neglecting the depression from 150–190° C., we get :—

(1) 100–240° C..... $A_l=2{\cdot}69 \,.\, 10^{-5}$; $B_l=1{\cdot}1 \,.\, 10^{-8}$.
(2) 250–280° C..... $A_l=1{\cdot}60(4) \,.\, 10^{-5}$; $B_l=3{\cdot}2(7) \,.\, 10^{-8}$.

Aluminium.

The results obtained at different times for aluminium, especially over the range 340–540° C., are somewhat at variance (*e.g.*, at 400° C. $\alpha \,.\, 10^{-5}=2{\cdot}855$, 2·894, 2·910, and,

* See Mellor, 'A Treatise on Inorganic Chemistry,' vii. p. 520.

several months later, 3·027, 3·196), but no systematic difference is found for the three separate sides of the cube. An explanation may lie in the fact that cold-worked aluminium recrystallizes slowly in a manner depending upon the temperature *.

The values given below are the mean linear coefficients of selected sets of results (see fig. 9) :—

Temperature v.	α_l.
100° C.	2·35(6) . 10^{-5}.
140° C.	2·43(6) ,,
180° C.	2·50(3) ,,
220° C.	2·57(3) ,,
260° C.	2·65(8) ,,
300° C.	2·74(4) ,,
340° C.	2·83(7) ,,
380° C.	2·88(9) ,,
420° C.	2·96(1) ,,
460° C.	3·01(7) ,,
500° C.	3·11(4) ,,
530° C.	3·23(3) ,,

Thiesen's Constants.—As an average for the whole range 100–530° C. we get :—

$$n=0{\cdot}384\ ;\quad K_l=2{\cdot}40\ .\ 10^{-6}.$$

The Constants of the Quadratic Relation.—For the range 100–530° C.,

$$A_l=2{\cdot}16(5)\ .\ 10^{-5}\ ;\quad B_l=9{\cdot}5\ .\ 10^{-9}.$$

Commercial aluminium was used for these measurements.

Brass.

Observations were taken up to 500° C. Up to 400° C. the maximum divergence from the mean values is about 1 per cent., but above 400 a 4 per cent. divergence is reached. The values given below are the mean linear coefficients :—

* See Mellor, ' A Treatise on Inorganic Chemistry,' v. p. 176.

Temperature v.	α_l.
140° C.	1·93(0) . 10^{-5}.
160° C.	1·97(1) ,,
180° C.	2·00(9) ,,
200° C.	2·04(2) ,,
220° C.	2·06(6) ,,
240° C.	2·08(8) ,,
260° C.	2·10(6) ,,
280° C.	2·12(8) ,,
300° C.	2·15(2) ,,
320° C.	2·18(0) ,,
340° C.	2·21(4) ,,
360° C.	2·25(1) ,,
380° C.	2·29(5) ,,
400° C.	2·35(4) ,,
420° C.	2·4(4) ,,
440° C.	2·5(6) ,,
460° C.	2·6(0) ,,
480° C.	2·5(6) ,,

These results do not fit either Thiesen's or the Quadratic formula. The rate of increase of α_l with temperature decreases until about 270–280° C., after which it increases, at first gradually, and later very rapidly. A maximum value for α_l occurs at about 460° C. (see fig. 9).

Common brass of 62 per cent. copper was used.

Copper.

Observations were taken up to 340–350° C. only. The mean results for the linear coefficients are (see fig. 9) :—

Temperature v.	α_l.
110° C.	1·66(3) . 10^{-5}.
120° C.	1·66(8) ,,
140° C.	1·68(0) ,,
160° C.	1·68(7) ,,
180° C.	1·69(3) ,,
200° C.	1·69(9) ,,
220° C.	1·70(7) ,,
240° C.	1·71(8) ,,
250° C.	1·72(2) ,,
260° C.	1·73(5) ,,
280° C.	1·74(0) ,,
300° C.	1·75(2) ,,

Thiesen's Constants.—For the range 110–300° C.,

$$n = 0{\cdot}112\ ;\quad K_l = 8{\cdot}53\,.\,10^{-6}.$$

The Constants of the Quadratic Relation.—For the range 110–300° C.,

$$A_l = 1{\cdot}62(3)\,.\,10^{-5}\ ;\quad B_l = 2{\cdot}0\,.\,10^{-9}.$$

Cobalt.

In the experiments with cobalt observations were taken from air temperature to about 730° C., and down again to about 100° C.

It was found that the coefficient of expansion during heating is different from that during cooling. Upon heating the coefficient increases slowly and regularly from air temperature to 390° C. At this temperature the coefficient increases rapidly to form a sharp peak with a maximum in the region of 450° C., where the coefficient is over twice that at the bottom of the peak. The base of the peak extends for 70–130° C. Above the region of the peak the curve continues sometimes with little variation in the coefficient, and sometimes with a small peak. The general characteristic of the expansion coefficient during cooling is that it decreases gradually down to about 360° C., where a peak commences. This peak has a height equal to about half that of the peak in the heating curve, and has its maximum in the neighbourhood of 330° C., *i. e.*, at a full 120 degrees below the maximum in the heating curve.

So far as can be ascertained, the peaks in the coefficient of expansion curves for cobalt have not previously been noted. They indicate the point at which some molecular change takes place. Honda and Shimizu* concluded that annealed cobalt undergoes a molecular change at 464° C., as the magneto-striction effect was then zero.

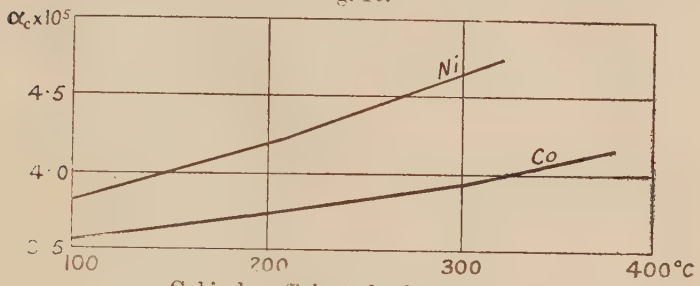
The results given below are the values for the volume coefficient from 100–380° C., during heating.

Temperature v.	α_c.
100° C.	3·55(6) . 10^{-5}.
120° C.	3·59(1) ,,
140° C.	3·62(6) ,,
160° C.	3·66(1) ,,
180° C.	3·69(6) ,,
200° C.	3·73(5) ,,
220° C.	3·77(5) ,,
240° C.	3·81(4) ,,
260° C.	3·85(3) ,,
280° C.	3·89(5) ,,
300° C.	3·94(2) ,,
320° C.	3·99(3) ,,
340° C.	4·04(3) ,,
360° C.	4·09(8) ,,
380° C.	4·15(0) ,,

* Phil. Mag. [6] vi. p. 392 (1903).

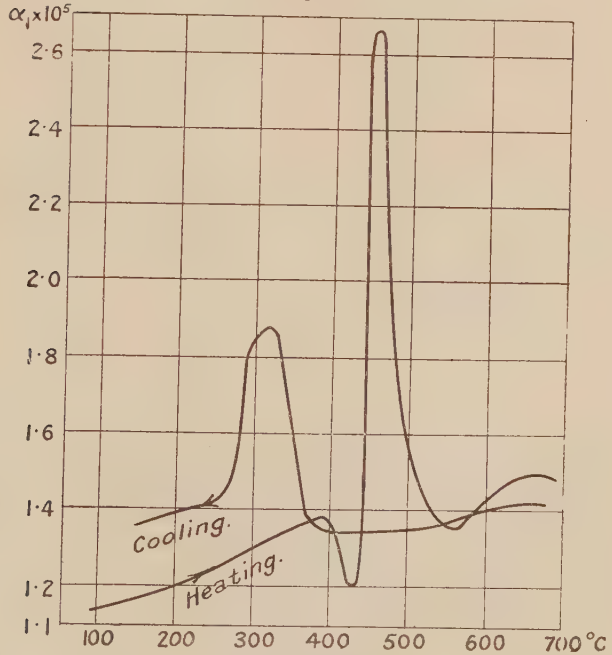
These results when plotted (see fig. 10) fall into three different straight lines. The points at which the changes of slope occur are (1) at about 190° C. and (2) from 260–300° C. Since the error of lag could not be completely

Fig. 10.



Cubical coefficients for Co and Ni.

Fig. 11.



Cobalt (side 3).

allowed for, however, these results are not so reliable as those for other metals.

The specimen set of results for cobalt given below is shown plotted in fig. 11.

Cobalt (side 3).—L=0·3990 cm.

Heating.				Cooling.			
N.	v, °C.	v (mean), °C.	α.	N.	v, °C.	v (mean), °C.	α.
0	29·62			141	723·54		
10	92·40	90	1·14(1) . 10^{-5}.	131	675·01	676	1·42(7) . 10^{-5}.
20	150·20	151	1·17(5) ,,	121	627·57	627	1·42(1) ,,
30	209·36	207	1·21(6) ,,	111	578·64	579	1·39(9) ,,
40	263·10	263	1·26(8) ,,	101	529·65	528	1·36(2) ,,
50	317·52	315	1·32(2) ,,	91	478·11	479	1·35(7) ,,
60	366·79	367	1·37(6) ,,	81	428·74		
70	417·15					406	1·34(9) ,,
73	434·18	426	1·20(7) ,,	72	383·03	363	1·37(9) ,,
75	443·21	439	1·51(8) ,,	66	353·21	343	1·63(8) ,,
77	447·48	445	3·20(7) ,,	61	332·30	323	1·87(4) ,,
		450	2·65(7) ,,				
80	455·09	451	2·69(9) ,,	56	314·02	305	1·87(7) ,,
85	469·35	462	2·40(0) ,,	51	295·77	286	1·80(4) ,,
90	488·43	478	1·79(4) ,,	46	276·77	265	1·49(3) ,,
95	510·64	500	1·54(1) ,,	41	253·78	230	1·41(1) ,,
100	535·16	525	1·39(6) ,,	31	205·19	181	1·38(8) ,,
111	591·23	586	1·41(4) ,,	21	155·74	133	1·35(1) ,,
121	636·84	637	1·49(6) ,,	12	100·00		
131	682·75	683	1·49(5) ,,				
141	728·43						

Nickel.

Observations were taken up to 710–720° C., with the exception of some early work, in which 770°C. was reached.

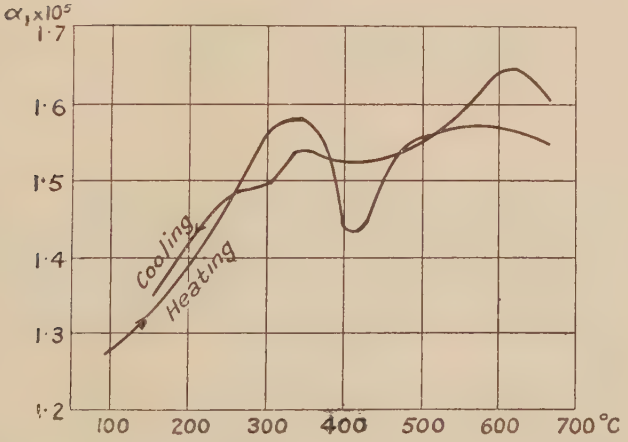
As in the case of cobalt, the rate of expansion is different from the rate of contraction for any definite temperature. During heating the coefficient increases fairly regularly from air temperature to form a shallow peak with its maximum at 340–360° C., above which the coefficient falls to form a minimum at about 420° C., and continues in an indefinite manner until the maximum temperature of the experiment is reached. In experiments in which the temperature of 770° C. was reached the coefficient increased regularly with temperature over this extended range both upon heating and upon cooling; this indicates

that nickel reaches a stable state above 700° C. The general characteristics of the cooling curve are, very approximately, that of the heating curve. Individual sets of observations vary greatly beyond the first minimum of the heating curve. The first maximum in the heating curve corresponds to the point at which nickel loses its ferro-magnetic properties.

The results for nickel during heating from 100–320° C. are :—

Temperature v.	α_c.
100° C.	3·81(7) . 10^{-5}.
120° C.	3·88(9) ,,
140° C.	3·96(0) ,,
160° C.	4·03(2) ,,
180° C.	4·10(7) ,,
200° C.	4·18(7) ,,
220° C.	4·27(4) ,,
240° C.	4·36(8) ,,
260° C.	4·46(1) ,,
280° C.	4·55(3) ,,
300° C.	4·64(7) ,,
320° C.	4·74(9) ,,

Fig. 12.



Nickel (side 1).

These values for α^c, when plotted against the temperature (see fig. 10), form two straight lines meeting just below 200° C. The error due to lag renders these results, like those for cobalt, less reliable than those for other metals.

The specimen set of results given below is shown plotted in fig. 12.

Nickel (side 1).—L=0·4060 cm.

Heating.				Cooling.			
N.	v, °C.	v (mean), °C.	α.	N.	v, °C.	v (mean), °C.	α.
3	42·92			150	707·59		
10	81·11	88	1·26(3) . 10^{-5}.	140	664·98	666	1·60(7) . 10^{-5}.
20	133·96	133	1·30(6) ,,	130	623·85	624	1·64(3) ,,
30	184·10	181	1·36(1) ,,	120	583·05	582	1·62(4) ,,
39	227·82	231	1·43(7) ,,	110	540·95	540	1·57(5) ,,
50	277·73	275	1·51(0) ,,	100	497·62		
60	321·34			90	453·98	476	1·54(2) ,,
70	363·86	343	1·58(2) ,,	80	409·79	432	1·52(4) ,,
77	394·27	379	1·54(8) ,,	70	365·71	388	1·52(8) ,,
78	397·26			60	322·00	344	1·54(1) ,,
90	453·41	425	1·43(7) ,,	49	272·42	297	1·49(4) ,,
100	497·01	475	1·54(2) ,,	40	231·47	252	1·48(1) ,,
110	539·34	540	1·56(6) ,,	31	189·08	210	1·43(3) ,,
120	582·89	582	1·57(1) ,,	17	119·21	154	1·35(3) ,,
130	624·97	626	1·56(6) ,,				
140	668·80	668	1·54(8) ,,				
150	711·88						

Steel.

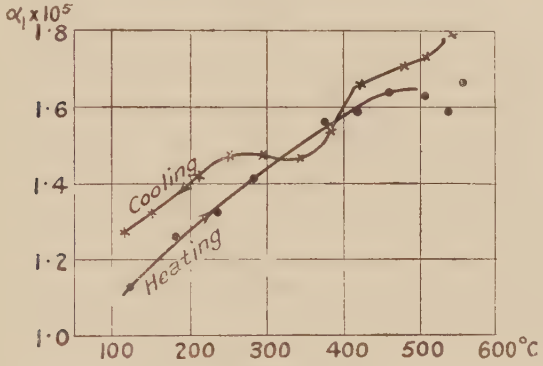
Fig. 13 is an example of the results obtained for a sample of steel which acted as the sole support of the upper interference plate. Frequent discontinuities in the extension curve make the results unreliable, but they serve to show a difference in the expansion coefficient during heating and cooling.

Summary of Results.

Tin, cadmium, and zinc show pronounced anisotropic properties, and over extended temperature ranges the cubical expansion coefficient curves fit neither the Quadratic nor Thiesen's formula. The expansion coefficient curve for lead has definite changes in slope at 170° and 245° C.; the mean aluminium and copper curves fit

the Quadratic relation, while that for brass with a maximum at 460° C. does not fit. For cobalt, nickel, and steel the expansion coefficient curve during heating is different from that during cooling, cobalt showing a sharp peak at 450° C. on heating, and at 330° C. on cooling; nickel has a maximum in the heating curve at 340–360° C. (the Curie point).

Fig. 13.



Steel.

Acknowledgment.

I wish to thank Professor C. H. Lees for much help and advice given throughout these measurements.

LXII. *X-Ray Study of some Tungsten Magnet Steel Residues.*

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[Plate V.]

Introduction.

THE nature of the carbide and other constituents of tungsten magnet steels has been the subject of much research. Thus Arnold and Read [1] isolated these constituents by dissolving away the iron electrolytically in dilute acid and collecting the insoluble remainder. From chemical analysis of the residues they inferred the presence of tungsten carbide, cementite, and free carbon, but found

* Communicated by G. W. C. Kaye, O.B.E., D.Sc.

no indication of a mixed carbide. Honda and Murakami [2], using their method of magnetic analysis, came to the conclusion that, in addition to those carbides in this type of steel, a mixed carbide, $4Fe_3C.WC$, also formed after certain heat treatments. Evershed [3] has published a very full survey of the problems arising in the manufacture of tungsten magnet steels. In it he states that the substances normally to be found in such steels are tungsten carbide and cementite, and that these compounds may decompose, apparently into their constituent atoms, when the steel has been "spoiled" by having been heated at about 950°C. Swinden [4], working on 3 per cent. tungsten steels, adduced evidence for the formation in normal steels of a compound of composition Fe_3W. In the case of high speed tool steels containing a large proportion of tungsten Westgren and Phragmèn [5], by using the method of X-ray analysis, proved that the carbide constituent consisted mainly of a mixed carbide, to which they assign the formula Fe_4W_2C, the metal atoms being to a slight extent mutually replaceable. The general lack of agreement concerning the nature of the constituents of magnet steels containing about 6 per cent. of tungsten is very evident, and is probably largely due to difficulties of interpretation inherent in the methods used.

X-ray analysis in this type of problem provides the most direct method of attack. It is possible by a straightforward photograph of the steel to obtain an X-ray diffraction spectrum of the carbide constituents superposed on the spectrum due to the iron. A difficulty appears, however, in the case of steels such as those investigated in the present work, because the proportion of any carbides will be small in comparison with the amount of iron present. Consequently an increase in exposure, made with a view to intensifying the carbide spectrum, merely results in such an increase of general X-ray scattering by the iron atoms that the weaker carbide lines are masked by the background of the photograph. It is therefore preferable to follow the process of Arnold and Read, and isolate the carbides by dissolving away the iron. The question then arises as to what extent the constituents of the residues as revealed by X-ray analysis are representative of the corresponding substances in the untreated steel. The degree of correspondence can be tested, however, by comparing the spectra of the residues, obtained under various conditions of

electrolysis, with the spectrum of the untreated steel. This latter, though less complete, is quite sufficient for the purpose. Evidence on this point is discussed in the paper.

Identification of the Residues.

The residues from some twenty steels were examined. Each had approximately the same composition as the following typical specimen: by weight, tungsten 6 per cent., carbon 0·72 per cent., nickel 0·19 per cent., manganese 0·28 per cent., silicon 0·14 per cent., sulphur 0·023 per cent., and phosphorus 0·027 per cent. Different steels had received different heat treatments. The residues from the steels gave diffraction spectra which were, with the reservations discussed below, very similar. For purpose of complete measurement two steels were chosen. They will be referred to as C1 and C3. The former had been heated for one hour and the latter for six hours at 900° C., and then allowed to cool in air. The surface of each was ground in order to remove the decarbonized layers. To obtain X-ray photographs of the residues a Debye camera was used. The radiation employed throughout is the iron Kα wave-length.

The problem then presents itself of identifying the carbides from the complicated spectrum arising from the probable presence of more than one constituent. Fortunately, advantage can here be taken of work by Dr. G. Shearer and the author—that, it is hoped, will soon be published—in which it was noted that variations in heat treatment of these steels resulted in large differences in the distribution of intensity amongst the lines of the spectra without alteration in their position. The same effect was reproduced in the spectra of the corresponding residues. The point is illustrated in Pl. V. figs. 1 and 2, which show the powder photographs of the residues C1 and C3 respectively. The measurements made from them are given in the table (p. 662). The lines are specified by the diffraction angle θ at which they occur. When a resolution of the Kα and α' doublet appears the angle for the α radiation alone is recorded. Column 1 gives the values of θ for the residue C1, and column 2 for C3. Here, again, the aforementioned point is illustrated. Nearly all lines, except very weak ones, are common to both; but while the positions are the same, the intensities of the lines do not correspond. Practically all the lines marked strong in the one are weaker when

Residue C1 θ (in degrees).	Residue C3 θ (in degrees).	WC θ (in degrees) (calc.)	Fe_4W_2C θ (in degrees). (calc.)
16·7 v.w.	—	—	16·9 v.w.
—	17·9 w.	18·0 w.	—
18·2 v.w.	—	—	18·2 w.
19·8 w.	19·8 s.	20·0 s.	—
20·3 v.w.	20·3 m.	20·4 m.	20·2 w.
20·5 w.	—	—	20·5 m.
22·4 m.	—	—	22·4 s.
22·6 w.	22·6 s.	22·6 s.	—
22·9 w.	—	—	22·9 m.
24·3 m.	24·3 w.	—	24.3 m.
25·3 s.	25·4 m.	—	25·4 s.
26·7 v.w.	—	—	26·7 w.
27·1 s.	27·1 m.	—	27·1 s.
27·8 v.w.	27·9 m.	27·8 s.	—
28·5 m.	28·5 w.	—	28·4 v.w.
29·7 s.	29·7 w.	—	29·7 s.
31·1 w.	31·1 s.	31·0 s.	—
33·0 w.	—	—	—
33·5 v.w.	—	—	33·7 v.w.
34·6 v.w.	—	—	34·6 w.
—	37·0 v.w.	36·7 w.	—
37·8 v.w.	—	—	37·7 w.
—	38·5 v.w.	38·2 v.w.	—
38·7 s.	38·8 w.	—	38·7 w.
40·5 v.w.	—	—	40·5 w.
42·2 w.	42·2 m.	41·8 s.	—
42·4 s.	42·4 v.w.	—	42·3 s.
—	43·0 v.w.	42·8 w.	—
43·3 v.w.	43·4 m.	43·2 m.	—
43·5 v.w.	—	—	43·5 v.w.
44·6 v.w.	44·6 v.w.	44·3 w.	44·5 v.w.
—	45·5 v.w.	45·3 m.	—
45·9 s.	—	45·8 v.w.	45·9 s.
48·0 s. 48·2 s.	48·1 m.	—	48·0 s.
48·8 w.	48·8 m.	48·5 s.	—
49·3 s.	49·3 w.	—	49·3, 49·4 m.
—	50·0 w.	49·8 w.	—
50·6 v.w.	50·6 m.	50·4 m.	—
51·4 w.	—	—	—
51·9 w.	51·9 s.	51·6 s.	—
52·3 v.w.	—	—	52·3 w.
53·0 w.	—	—	52·8, 53·0 w.
54·0 w.	—	—	54·1 w.
55·3 m.	55·2 v.w.	—	55·2 m, 55·4 w.
57·8 w.	57·8 m.	57·2 w.	—
60·6 s.	60·5 m.	—	60·5 s.
60·8 s.	60·8 m.	—	60·7 s.
63·2 s.	63·1 w.	—	63·1 s.
63·4 s.	63·4 w.	—	63·4 s.
64·3 w.	—	—	—
65·0 s.	65·0 m.	—	65·0, 65·1 s.
66·3 w.	—	—	—
67·8 w.	67·8 w.	67·5 w.	67·8 w.
73·2 m.	73·2 s.	72·4 s.	—

v.w. = very weak intensity, w = weak, m = medium, s = strong.

they occur in the other. It is therefore possible to isolate a set of lines, belonging presumably to one substance, which on going from C1 to C3 increase in intensity. These lines correspond to the known spectrum of tungsten carbide. This is shown in column 3, which is arranged so that opposite these lines are placed the values of the diffraction angles for tungsten carbide as given by Westgren and Phragmèn [6] in their research on the tungsten-carbon system. A comparison of the columns shows definitely the presence of tungsten carbide in both residues with a preponderance in C3. A closer examination of the diffraction angles observed for tungsten carbide is made below. First we proceed to isolate a second set of lines, namely, those which on going from C1 to C3 decrease in intensity. Here, again, a correspondence was obtained with the diffraction angles of a substance the crystal structure of which has been determined. The values of the angles for this substance, the mixed carbide Fe_4W_2C, are given in column 4. They are arranged, for ease of comparison, so as to be on the same row as the lines in the residues to which they correspond. In order not to confuse this arrangement a few of the calculated values of the angles for the mixed carbide, which correspond to lines which are very weak and were not observed, are omitted. The agreement of the large number of lines in column 4 with those isolated in the above procedure proves definitely the presence of the compound Fe_4W_2C. That the residues consist, therefore, of a mixture of the double carbide Fe_4W_2C and tungsten carbide in varying proportions would accord with the observed spectra. There are, however, five lines unaccounted for in the C1 residue. One, at $\theta = 28°{\cdot}5$, is too strong for the known spectrum of Fe_4W_2C. The others, at $\theta = 33°{\cdot}0$, $51°{\cdot}4$, $64°{\cdot}3$, and $66°{\cdot}3$, do not occur at all in the above carbides. These lines do not fit on a simple structure, and are too few to afford information about a complicated one. They do not correspond to lines which would be produced by the presence of cementite, of the compound W_2C, or of free carbon. The residue of a steel containing an enhanced proportion of silicon (1·05 per cent.) also gave these lines, and they were stronger in proportion, thus suggesting that they are due to a silicon compound as yet unidentified.

Closer examination of the carbides reveals interesting information. In the case of tungsten carbide a definite

discrepancy is evident between the values of the larger glancing angles observed and those published by Westgren and Phragmèn. That this difference exceeded experimental error was shown thus :—A section of the magnet bar C3 was sawn, and filed into the form of a thin rod, and then reduced by dissolving away the surface electrolytically in dilute hydrochloric acid until a very thin wire remained. The diameter of this wire was made as nearly as possible the same as that of the powder which was used in the Debye camera, so that a photograph of the wire could be secured under the same conditions as those obtaining in the case of the residue photographs. A reproduction is shown in Pl. V. fig. 3. Measurements of the positions of the iron lines then afforded an accurate means of checking the spacings of the tungsten carbide lines which occurred on the same photograph. It was found that the latter, like the corresponding lines in the residues, still exhibited the small deviation in spacing from the results given by Westgren and Phragmèn. On the other hand, a comparison photograph of tungsten carbide obtained from other sources gave results agreeing with those of Westgren and Phragmèn. Moreover, it was observed that in certain residues, generally those in which the mixed carbide lines were weak, the intensity of one or two lines was increased disproportionately when compared with a photograph of the normal tungsten carbide. In consequence, one is led to conclude that the tungsten in the tungsten carbide is to some extent replaceable, probably by iron, a smaller atom. This would then explain the slight decrease in the size of the tungsten carbide lattice.

In the case of the mixed carbide, Fe_4W_2C, it was found that, on comparing the photographs of residues from differently heat-treated steels, definite variations in the relative intensities of the lines were noticeable. This suggests the possibility of a slight disturbance of the arrangement of the atoms in the unit-cell, due either to atomic replacement or the interpenetration of a foreign atom.

The Validity of the Residue Method.

Photographs of steels C1, C3, and others, reduced to the form of wires in the manner described above, were obtained in the Debye camera, together with comparison-photographs of residues from the same steels. Preliminary

work showed that the spectrum was not affected by reducing the steels to this shape. A set of residues from each steel was prepared by the use of current densities of 0·4, 0·1, 0·05, and 0·001 amp. per sq. cm. respectively passed through hydrochloric acid of specific gravity 1·014. A comparison of the residue and the steel photographs was carried out, and the following conclusions were arrived at:—

Firstly, a few lines often occurred on the residue photographs which were absent from the corresponding steel photograph, despite the fact that they were of sufficient intensity in the former to warrant their appearance in the latter. They are, therefore, presumably due to spurious products formed in the process of electrolysing. In order to secure sufficient residue for purpose of chemical analysis, the conditions would appear to be such as to permit of the formation of foreign products, which would invalidate conclusions based on such analysis. The method of X-ray analysis, however, has the advantage that a spectrum from the source of the residues can be used to check the residue spectrum, and thus extraneous effects can be eliminated.

Secondly, it was found that the relative proportions of tungsten carbide and the double carbide present in the residue from a given steel varied with different electrolysing conditions. A chemical analysis was made of two such residues, which showed a slight difference in proportion of the carbides present. The results of the analysis of each residue were very different. This, suggests, again, that the results obtained by the chemical method are much more difficult to interpret than X-ray results.

Thirdly, it was found that the breadth of the carbide lines, which depends on the average particle size, as observed in a steel spectrum and in the corresponding residue spectrum, is the same. As an extreme case it was observed that in some steels no carbide spectrum at all appeared, from which one concludes that the carbide crystals are so small as to be practically amorphous. In such cases it appeared that the corresponding residue also yielded no X-ray pattern. Here, of course, the X-ray method can give no clue to the chemical nature of substances present, but it does illustrate the state of carbide subdivision in a region inaccessible to optical microscopy. When steels in which the carbides are amorphous are heated at 900° C. there is a tendency for the carbide particles to grow. Invariably in such steels the carbide

spectra gave strong sharp lines. But similar heating of the amorphous residues *in vacuo*, in air, or in argon, with a view to crystallizing them, did not produce these carbides. Instead, other substances formed, as yet unidentified. This would suggest that the amorphous residues do not contain the same compounds as the crystalline ones ; but further work on this point is needed and will be undertaken.

The above results would seem to indicate that the method of chemical analysis of residues as a guide to the nature of steel constituents is of doubtful value. The method of X-ray analysis, on the other hand, appears to be quite reliable provided that control photographs of the untreated steel are utilized in determining the correct conditions of electrolytic separation and the choice of electrolyte.

In conclusion, the author wishes to express his thanks to Mr. J. R. Clarkson for help in the preparation of many residues. He is also indebted to Dr. G. Shearer for his helpful interest in the work, and to Dr. G. W. C. Kaye for his interest and the facilities which have made the work possible. The steels were supplied by Dr. W. H. Hatfield in connexion with a wider research on the magnetic spoiling of tungsten steels.

Summary.

1. The carbide constituents of tungsten magnetic steels are identified from the X-ray spectra of the residues. They are tungsten carbide, the mixed carbide Fe_4W_2C, and a third compound probably due to the silicon content. No cementite is found.

2. The tungsten carbide spacings are found to be slightly smaller than the normal values. In this, as well as in the mixed carbide, it is suggested that atomic replacement occurs.

3. Chemical analysis of the residues as an indication of steel constituents is found to be of doubtful value. X-ray analysis is shown to be reliable when controlled by photographs of the untreated steel.

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LXIII. *The Electrical Properties of the Soil at Radio Frequencies.*

By J. A. Ratcliffe, *M.A., and* F. W. G. White, *M.Sc.* (*Strathcona Research Student, St. John's College, Cambridge*), *Cavendish Laboratory, Cambridge* *.

I. *Introduction.*

RECENTLY two methods have been developed by means of which the influence of the earth on wireless waves may be investigated. In one of these the attenuation of the waves is measured as they pass over the surface of the earth, while in the other the tilt of the wave-front is measured. The results of both classes of experiment have always been expressed in terms of a conductivity (σ) and a dielectric constant (ε) for the soil considered. In this paper it is pointed out that, on theoretical grounds, we should not expect the quantities σ and ε to be constant, but we should expect them to vary with the frequency of the waves used.

In order to investigate how serious this variation may be, samples of soil have been investigated, in the laboratory, by two methods. The results of these experiments show that the variations may be considerable as we pass from one wave-length to another. We shall show, in paragraph II., that the fact that σ and ε are not constant leads to difficulties in the interpretation of the attenuation experiments. After describing the laboratory experiments in paragraphs III., IV., and V., we shall, in paragraph VI., apply our results to a fuller discussion of these difficulties.

II. *Difficulties resulting from the Variation of the Ground Constants.*

The purpose of experiments in which the attenuation of wireless waves is measured has been twofold. Firstly,

* Communicated by Professor E. V. Appleton, F.R.S.

they were carried out in order to verify the theories of propagation over the earth, which have been worked out by Zenneck * and Sommerfeld †; and, secondly, they were made to determine the electrical properties of the ground, so that its behaviour might be foretold in the future. The fact that the effective dielectric constant and conductivity of the ground may change with the frequency of the applied e.m.f. leads to considerable difficulties in the interpretation of attenuation experiments in the following three ways.

1. In the attempted verification of Sommerfeld's theory the method which has sometimes been used is that of making attenuation measurements on two different wave-lengths, and from them deducing the values of σ and ε in the two cases. If the results were the same in the two cases, it has been thought that the theory is verified. We now see, however, that we should not necessarily expect to obtain the same values of σ and ε on two different wave-lengths, so that this method of verification is not satisfactory.

2. It has often been assumed that if σ and ε have been measured for a certain wave-length then the attenuation of waves of different wave-length may be foretold by the applications of Sommerfeld's calculations. Thus Rolf ‡, working on this assumption, has drawn up a series of curves to show how it is possible, given the attenuation of waves at one frequency, to deduce that at all other frequencies. It is interesting in this connexion to note that Rolf says that "Measurements known to the author [Rolf] give no evident reason for further complicating the theory by introducing variable constants of the soil." He also says that "The main task in the near future is to show by comparison between theory and experiments that these characteristic constants of the earth's surface are really constant, and not dependent upon wave-length." If the "constants" do, in fact, vary with frequency, curves of the kind mentioned above must be used with great care, and extrapolations to very different wave-lengths must not be made.

3. It has also been pointed out recently § that an explanation of the anomalous "negative attenuation"

* *Ann. der Phys.* xxiii. p. 846 (1907).
† *Ann. der Phys.* xxviii. p. 665 (1908).
‡ Proc. Inst. Radio Engs. xviii. p. 391 (1930).
§ 'Nature,' p. 926 (June 21, 1930).

effect noticed by Ratcliffe and Barnett * can be given if we may assume that $\sigma = 7 \times 10^{-15}$ e.m.u. and $\varepsilon = 80$ e.s.u. for the ground considered. These values differ widely from those to be expected as a result of measurements on other frequencies. How are we to know whether or not these apparently "abnormal" values are the correct deduction from the attenuation experiments, or whether some other disturbing factor is influencing the propagation? We shall be helped to a decision by a laboratory investigation of how the properties of the ground change with frequency.

III. *Theoretical Considerations.*

Before describing the experimental procedure in detail we will discuss a few fundamental points underlying the theoretical work of Zenneck and Sommerfeld.

When a wave passes over the ground it induces in it currents which are due to all or any of the following causes :—

(*a*) a displacement current in the æther between the soil molecules ;

(*b*) movements of bound charges in the soil molecules ;

(*c*) orientation of polar molecules ;

(*d*) movements of free "electrolytic" ions in crystals, moving under a frictional force, as shown by Joffe †;

(*e*) movements of electrolytic ions in solution.

The resultant current will not necessarily be in phase with the e.m.f. producing it, and, on account of the complicated nature of the conduction, the magnitude of the current and its phase relation to the e.m.f. will depend on the frequency.

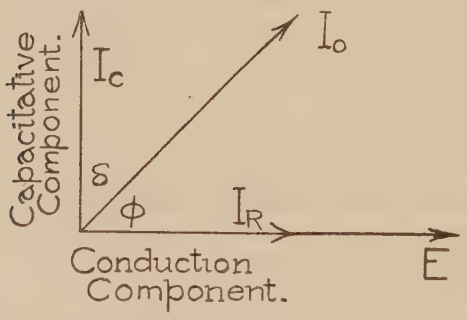
At any given frequency we can resolve the current into a component I_R in phase with the e.m.f. and a component I_C in quadrature with the e.m.f. (fig. 1). The in-phase component is called the conduction component and the quadrature component is called the capacitative component. Considering only I_R, we should say that the soil acted like a substance with conductivity σ where $\sigma = \frac{I_R}{E}$,

* Proc. Camb. Phil. Soc. xxiii. p. 288 (1926).

† 'The Physics of Crystals.'

while if we consider I_C alone we should say that it acted like a substance with dielectric constant ε, where ε is defined by $I_C = -\frac{\varepsilon}{4\pi}\frac{\partial E}{\partial t}$. In this way we are led to think of the current flowing in the soil at any given frequency as made up of these two components, although the physically important fact is that a current of magnitude I_0 flows and makes a phase angle of ϕ with the e.m.f. The results of experiments described in this paper show that the phase and magnitude of the current in a given sample of soil change with frequency, so that the "conductivity" σ and the "dielectric constant" ε are functions of the frequency of the applied e.m.f. and are not constant.

Fig. 1.



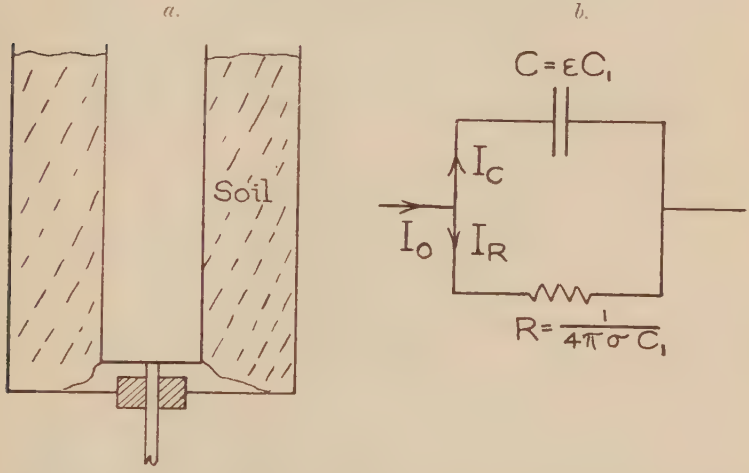
If, therefore, we still wish to describe the electrical properties of the soil in terms of σ and ε, it is more satisfactory to speak of these quantities as the "effective conductivity" and "effective dielectric constant" respectively. It often happens, however, that it is more convenient to describe the electrical properties of the soil in terms of the phase angle ϕ and the effective dielectric constant ε. This is more particularly the case since the publication of Rolf's valuable series of attenuation curves, which he expresses in terms of ε and a quantity $\tan b$, where $\tan b = \frac{n(\varepsilon+1)}{2\sigma}$ (n = frequency of the wave). If ε is large, as it is in the case under consideration, we have the approximate relation $\tan b = \tan \phi$. We shall see that

tan ϕ is a quantity which is directly measured in one of our experiments, and we have expressed our results in terms of ε and tan ϕ. For comparison with previously determined values of σ we have also given the values of σ for the different frequencies.

IV. *Experimental Arrangements.*

The soil was used as the dielectric between the plates of a cylindrical condenser, as shown in section in fig. 2, *a*. This

Fig. 2.



soil condenser may be replaced, for the purpose of explanation, by a perfect condenser with a dielectric of effective dielectric constant ε, in parallel with a resistance of effective value R (fig. 2, *b*). A knowledge of R will give the effective value of σ if we know C_1, the geometric capacity of the cylindrical condenser, since $R = \frac{1}{4\pi\sigma C_1}$. If C_s is the capacity of the soil condenser, we then have

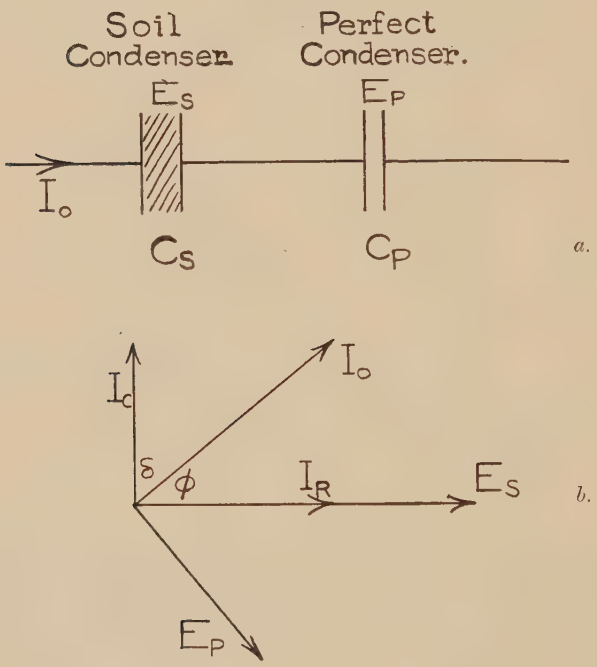
$$\tan\phi = \frac{I_C}{I_R} = R\omega C_S = \frac{\epsilon\omega}{4\pi\sigma} \quad \text{and} \quad \epsilon = \frac{C_S}{C_1}.$$

Two methods of investigation were used, and will be described separately.

The Oscillograph Method.

If the soil condenser is placed in series with a perfect condenser (capacity C_P) and an alternating current I_O passed through both (fig. 3, *a*) the vector diagram will be as in fig. 3, *b*. The e.m.f. E_S across the soil condenser will be in phase with the resistance component of the current I_R, while I_O will be ahead of E_S by the angle ϕ. The e.m.f.

Fig. 3.

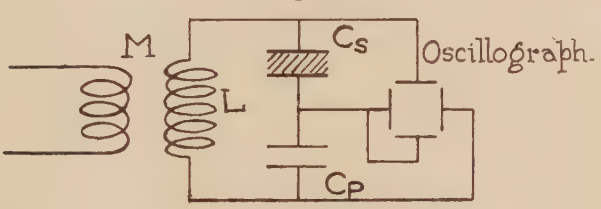


across the perfect condenser will be 90° behind I_O, and will lag behind E_S by the angle δ, which is also the angle between I_O and I_C. Thus, we can find δ and hence ϕ by investigating the phase difference between the e.m.f. across the soil condenser and that across the perfect condenser. This measurement is made by means of a cathode-ray oscillograph as shown in fig. 4. Current is caused to flow through the two condensers by loosely coupling the circuit

L C_P C_S to a source of radio-frequency current. The amplitudes of E_S and E_P can be made approximately the same by adjusting C_P. Precautions were taken to see that everything was working as expected. Substitution of other components, such as resistances and inductances, for C_S gave the correct oscillograph figure. Stray effects were eliminated by keeping the leads to the oscillograph as short as possible, while the coupling coils were placed at a sufficient distance to prevent magnetic deflexions of the cathode ray beam. It was demonstrated that any good mica condenser was sufficiently perfect to be used as the comparison condenser at C_P. Values of $\tan\phi = \tan(90-\delta)$ are obtained simply by tracing the elliptic pattern on the oscillograph screen and measuring it.

The advantage of this method lies in the fact that $\tan\phi$ can be obtained directly from the oscillograph trace. In

Fig. 4.



order to obtain values for the effective conductivity and the effective dielectric constant it would be necessary to measure the current through, and the e.m.f. across, the soil condenser at the same time as $\tan\phi$ was measured. Several values were determined and found to be of the same order as those found by the resonance method to be described below. The accuracy with which $\tan\phi$ can be obtained was limited by the method of tracing the ellipse on tissue paper in a dark room. Probably better results would be obtained by photographing the trace, but the accuracy obtained was sufficient for the present purpose.

Resonance Method.

The circuit used in the resonance method is shown in fig. 5. It is a tuned resonance circuit in which the capacity consists of a calibrated variable air condenser C_A in

parallel with the soil condenser C_s. An e.m.f. is induced from a radio-frequency source by way of the mutual

Fig. 5.

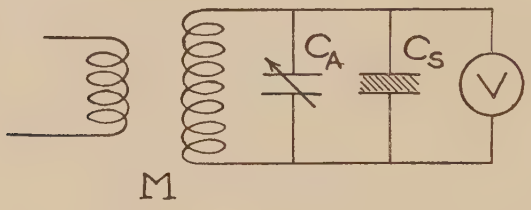
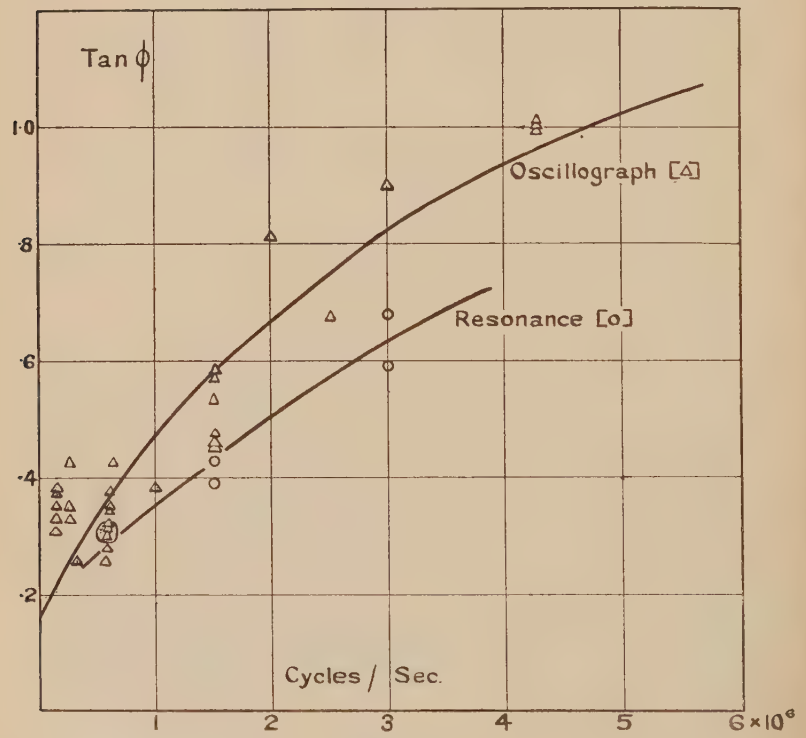


Fig. 6 *a*.

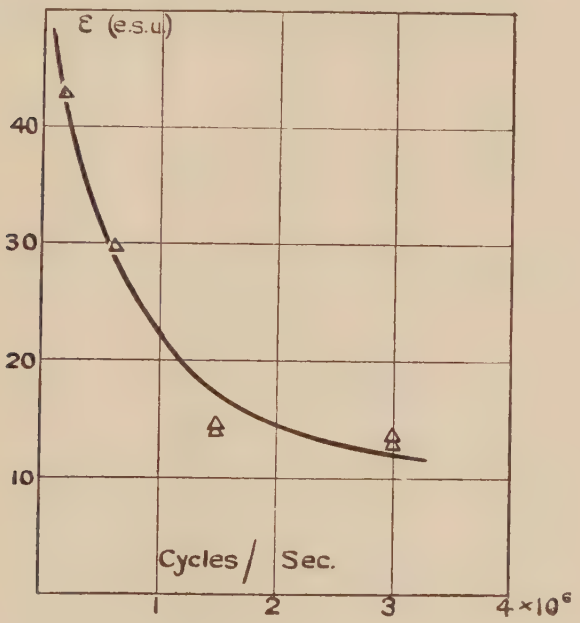


Cambridge soil.

inductance M. A Moullin voltmeter V measures the radio-frequency e.m.f. across the soil condenser.

To make a measurement the source is adjusted to provide an e.m.f. of the required frequency, the soil condenser is removed, and the air condenser is adjusted to give voltage resonance, as shown by the voltmeter. The soil condenser is now placed in parallel with the air condenser, and the latter is again adjusted to give voltage resonance. The difference between the two readings of the air condenser gives the effective capacity of the soil condenser.

Fig. 6 *b*.



Cambridge soil.

From a knowledge of the geometric capacity of the soil condenser the effective dielectric constant ϵ can be found.

A voltage resonance curve is now plotted, with the soil condenser in position, by varying the capacity C_A. If C_a and C_b are the values of C_A at the points where the e.m.f. across the condenser is $1/\sqrt{2}$ times the maximum e.m.f., and if we write $\Delta C = (C_a - C_b)$, then it can be shown that

$$\tan\phi = R\omega C_S = \frac{2C_S}{\Delta C} \quad \text{and} \quad \epsilon = \frac{C_S}{C_1}.$$

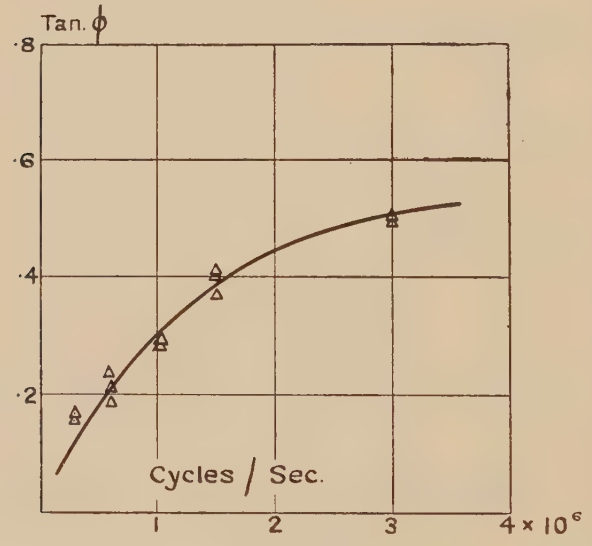
In this way ε and $\tan\phi$ are found.

There are certain limitations to the use of this method. At low frequencies the decrement becomes too high to allow a good resonance curve to be obtained, while at very high frequencies the magnitudes of ΔC and C_S become small. It has proved useful for frequencies between $0{\cdot}2 \times 10^6$ and 5×10^6 cycles per second.

V. *Experimental Results.*

Two types of soil were experimented upon, these being garden soil from Cambridge and surface soil from near

Fig. 7 *a*.

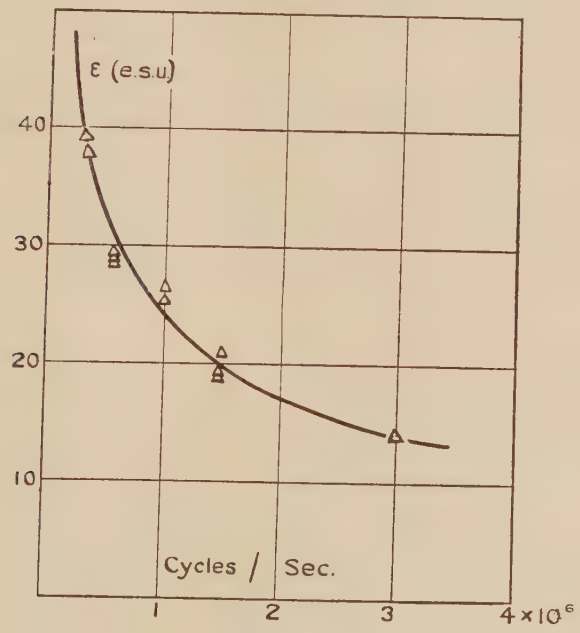


Daventry soil.

the Daventry Broadcasting Station. Figs. 6 *a* and 6 *b* show how the values of tan ϕ and ε for the Cambridge soil vary with frequency, while figs. 7 *a* and 7 *b* show the results for the Daventry soil. At high frequencies ϵ assumes a low limiting value which remains approximately the same up to a frequency of 10×10^6 cycles per second—a value not shown on the curves. For lower frequencies, however, the value of ε increases, becoming three or four times its value at the higher frequency. Although the two specimens

appear to be of very different physical and chemical constitution, the results obtained are similar. This is probably due to the fact that the moisture content of the soil plays a large part in determining its electrical properties. In order to investigate this point the same specimen of Daventry soil which was used to obtain fig. 7 was dried and again used as the dielectric. It was found that ε (at

Fig. 7 *b*.



Daventry soil.

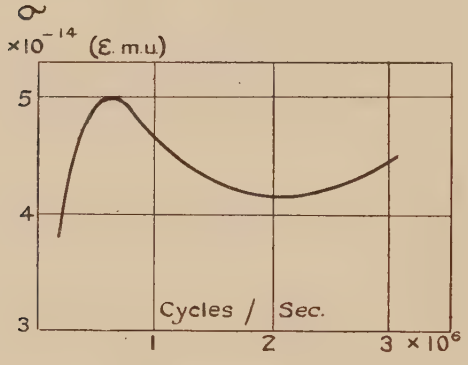
$0{\cdot}2 \times 10^6$ cycles per second) had decreased from 48·5 to 5·3, while $\tan\phi$ increased from 0·14 to 1·25. A similar change was also found as the amount of solid rock in the soil was increased.

Although $\tan\phi$ and ε are of primary importance from the point of view of attenuation experiments, it is interesting to note the variation that takes place in the effective conductivity σ. The curves (figs. 8 *a* and 8 *b*) have been

calculated from the smoothed curves of $\tan\phi$ and ε, by writing

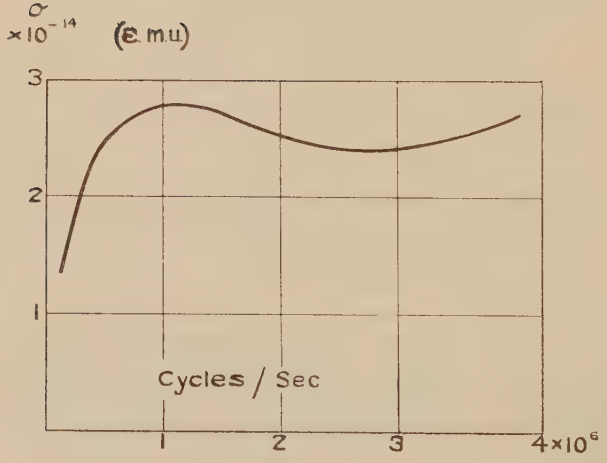
$$\sigma = \frac{\epsilon\omega}{4\pi\tan\phi}.$$

Fig. 8 *a*.



Daventry soil.

Fig. 8 *b*.



Cambridge soil.

VI. *Discussion of Results.*

The measurements have shown that the values of ε and σ change very considerably as the frequency of the

wave is changed. We will now apply this experimental result to a consideration of the three fundamental difficulties mentioned in paragraph II.

(1) In the confirmation of Sommerfeld's theory we now see that it is not sufficient to obtain attenuation curves on two different wave-lengths and expect to arrive at the same values of σ and ε. Since also σ and ε are different for different samples of soil, it is not possible to attempt a verification of Sommerfeld's expression by deducing the values of these quantities from an attenuation curve and then comparing them with the values found for a specimen of soil in the laboratory. The values of σ and ε found from the attenuation curve are undoubtedly average values for a layer of soil the thickness of which is of the order of one wave-length. It appears that the only possible method of verification is to measure the effective values of σ and ε for the ground *in situ* at the same frequency, and under conditions where the penetration of the wave is of the same order as in the attenuation experiments. The only method available for this determination is that of measuring the tilt of the wave-front as developed by Barfield.

(2) The method of predicting the attenuation of waves of one frequency from a knowledge of the attenuation at another frequency, assuming σ and ε to remain constant, now appears to be fundamentally incorrect. As an example of the kind of errors into which the procedure will lead us we will suppose that σ and ε have been measured at a wave-length of 100 metres, and have been found to be 10^{-14} e.m.u. and 10 e.s.u. respectively. If we then assume that the quantities remain constant as we change the wave-length to 1600 metres, we deduce an attenuation factor at a distance of 100 wave-lengths from the transmitter of 0·32 at the new wave-length. If, however, we take the value of ε to be 45 on the new wave-length, we deduce a value of 0·5 for this attenuation factor. This illustrates the kind of error into which we may be led if we neglect the variation of ε with frequency.

(3) The values of $\sigma = 7 \times 10^{-15}$ e.m.u. and $\varepsilon = 80$ e.s.u. required for an explanation of the "negative attenuation" effect on 1600 metres are not very far removed from those obtained in the present experiments, $\sigma = 4 \times 10^{-14}$, $\varepsilon = 45$. Considering the possible variations of soil properties with depth, it appears reasonable to suppose that the values

$\sigma = 7 \times 10^{-15}$ e.m.u. and $\varepsilon = 80$ e.s.u. are the correct deductions from the attenuation experiments. Experiments are being carried out to test this conclusion further.

The value of the effective dielectric constant ε has been found previously by Ratcliffe and Shaw * by means of attenuation measurements made at Cambridge using a wave-length of 30 metres. They found $\varepsilon = 20$ e.s.u. The present results for the Cambridge surface soil give a value $\varepsilon = 13$ e.s.u. In view of the probable variation of ε with depth, this is considered to be as close a confirmation as could be expected by this method. It is interesting to note that the value for ϵ deduced from the attenuation curve is higher than that deduced from the surface sample of soil both for 1600 and for the 30 metre measurements. This is possibly due to the fact that the deeper layers of soil may have a higher water content than the superficial layers.

In view of the very large values which have been obtained for the effective dielectric constant of the soil at the lower frequencies, it is of interest to inquire whether other investigators have noticed this effect. Bairsto † has investigated the dielectric constant and conductivity of slate at different frequencies, and has found values very similar to those which we find for soil. His values for ε are 10 e.s.u. at a frequency of 10^6 cycles per second, 16 e.s.u. at 100,000 cycles per second, and 40 e.s.u. at 3000 cycles per second. The variation in conductivity is also in the same direction as that observed by Bairsto.

VII. *Summary.*

Laboratory experiments have been made at radio-frequencies to investigate the way in which the effective conductivity σ and the effective dielectric constant ε of the soil vary with frequency. The results of the experiments are shown in figs. 7 and 8. The bearing of these results on some problems of the propagation of wireless waves is discussed, and the conclusion is reached that the only satisfactory way of measuring these quantities is to measure them for ground *in situ* and at the frequency required, either by the tilt method or by means of attenuation curves.

* 'Nature,' cxxiv. p. 617 (1929).
† Proc. Roy. Soc. xcvi. p. 363 (1912).

LXIV. *The Relations of the Magnetic and Thermal Constants of Ferromagnetic Substances.* *By* J. R. Ashworth, *D.Sc.**

Index to Paragraphs.

1. The object of the paper.
2. Curie's Law and Constant.
3. Development of the ferromagnetic equation and its constants.
4. Energy equation to ferromagnetism.
5. Relations of a' to R′ and θ to I_0.
6. The specific heat C_θ and its discontinuity Δc at the critical temperature, and their relations to the ferromagnetic constants.
7. Relation of Δc to C_θ.
8. Remarks on these relations.
9. Ratios of constants in groups of the ferromagnetics.
10. Table of fundamental quantities and constants.
11. Summary of equations.

1. In the general equation to ferromagnetism, which treats intensity of magnetization as a function of field-strength and temperature, three fundamental constants appear. If the equation is written in terms of energy it is at once allied to certain thermal quantities, and is amenable to thermal considerations. It is the object of this paper to present some relations which exist between the ferromagnetic constants themselves and between their allied thermal constants amongst the available substances which exhibit magnetic properties in a high degree. The ferromagnetic substances here considered are iron, cobalt, nickel, Heusler's alloy, and magnetite.

2. Curie's investigation † of the magnetic behaviour of diamagnetic, paramagnetic, and ferromagnetic substances under the influence of high temperatures laid the foundation for the modern theory of the relation of magnetism to temperature and led to the law and the constant which goes by his name. His researches at temperatures above the magnetic critical temperatures showed that the product of the susceptibility and the absolute temperature was constant for each ferromagnetic substance, but different for different substances. Calling this constant A, we have

$$A = kT, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the magnetic susceptibility and T the absolute

* Communicated by the Author.

† 'Œuvres' de P. Curie, 1908.

temperature. If I is the intensity of magnetization, that is, magnetic moment per unit volume, and H is field-strength, the equation can be put

$$\frac{H}{I} = \frac{T}{A} \quad \text{or} \quad \frac{H}{I} = R'T, \quad . \quad . \quad . \quad . \quad (2)$$

where R′ is the reciprocal of Curie's constant A. This is the paramagnetic equation. Curie pointed out that this equation is analogous to the gas-equation

$$PV = RT \quad \text{or} \quad \frac{P}{\rho} = RT, \quad . \quad . \quad . \quad . \quad (3)$$

where ρ is the density, which is inversely as the volume V, P is the pressure, and R is the well-known gas-constant. Thus H, I, and R′ correspond respectively to P, ρ, and R, while in both T is the absolute temperature.

3. Curie further pointed out that the passage of a ferromagnetic from paramagnetism to strong magnetism through the critical temperature is like the passage of a fluid from a gas to a liquid through its critical temperature, so that it is an obvious step to extend the paramagnetic equation into a more general equation to include ferromagnetism, just as van der Waals extended the gas equation to include liquids. Van der Waals's equation takes account of the mutual attraction of the molecules, which acts like an internal pressure, and of the finite size of the molecules which sets a limit to the density; and as ferromagnetism is distinguished from paramagnetism by the mutual action of the magnetic molecules, and the fact that the intensity has a limiting value, it follows that the ferromagnetic equation may be written on the model of the fluid equation, thus:

$$(H + a'I^2)\left(\frac{1}{I} - \frac{1}{I_0}\right) = R'T. \quad . \quad . \quad . \quad . \quad (4)$$

Here a' is the intrinsic field constant analogous to van der Waals's a, and I_0 is the limiting intensity of magnetization, so that $\frac{1}{I_0}$ is analogous to van der Waals's b*.

This equation is a cubic in I, and we can proceed to treat it after the manner of van der Waals's equation. For example, the critical values of H, I, and T can be written

$$H_c = \frac{a'I_0^2}{27}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* Ashworth, Phil. Mag. xxx. p. 711 (Nov. 1915).

$$I_c = \tfrac{1}{3} I_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\theta = \frac{8}{27} \frac{a' I_0}{R'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the evaluation of a' the equation to the critical temperature is most suitable. The two other constants I_0 and R' can be obtained by direct experiment. Values for the constants a', I_0, and R', with others, will be found at the end of this paper for all the ferromagnetics.

4. The equations to paramagnetism and to ferromagnetism are susceptibility equations, whilst the gas and fluid equations are energy equations. It is easy, however, to pass from a susceptibility equation to an energy equation for magnetism. In the paramagnetic state, where the mutual action of the molecular magnets is absent, we have

$$\frac{1}{k} = R'T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

which becomes

$$\frac{I_0^2}{k} = R' I_0^2 T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

on multiplying throughout by I_0^2.

The left side is an expression for maximum work when H is constant and T variable. The equivalent thermal energy is that of two degrees of freedom of kinetic energy, which may be written RT, and consequently

$$\frac{I_0^2}{k} = R' I_0^2 T = RT,$$

from which we get

$$R' I_0^2 = R, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where R is in mechanical units and is referred to unit volume.

Thus by multiplying by I_0^2 we can pass from a susceptibility equation to an energy equation. We can then write for the ferromagnetic energy equation

$$I_0^2 (H + a' I^2) \left(\frac{1}{I} - \frac{1}{I_0} \right) = R' I_0^2 T, \quad . \quad . \quad (11)$$

or more conveniently,

$$(H I_0 + a' I_0 I^2) \left(\frac{I_0}{I} - 1 \right) = RT, \quad . \quad . \quad . \quad (12)$$

where the first bracket represents energy in terms of

magnetism and the second bracket has only numerical significance. The equation to the absolute critical temperature (θ) becomes

$$\theta = \frac{8}{27}\frac{a'I_0^3}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

or

$$R\theta = \frac{8}{27}a'I_0^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Equation (10), namely,

$$R'I_0^2 = R,$$

is one connecting constants which can be separately determined, and its truth can thus be readily tested. It can, however, be used in turn for the evaluation of any of the constants, and is convenient for the determination of I_0. The values of I_0 in the table at the end of this paper have been so determined, except those for Heusler's alloy and for magnetite.

The constant R as used above refers to the kinetic energy per degree centigrade in mechanical units for two degrees of freedom per cubic centimetre. If the gas constant has the usually accepted meaning of $83{\cdot}15 \times 10^6$ ergs per degree centigrade for a gram molecule, then we must substitute for R in the formula the term $\frac{R}{an}$ to make it apply to one gram, and $\frac{R}{an}\rho$ for one cubic centimetre of volume, where a is the atomic mass, n the number of atoms in the molecule, and ρ the density of the material. Thus

$$R'I_0^2 = R\frac{\rho}{an} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The application of this equation for the evaluation of I involves a knowledge of n, but this presents no difficulty, as n must be a small number, and can be determined by inspection. Thus for iron we have

$$I_0^2 = \frac{R}{an}\frac{\rho}{R'} = \frac{83{\cdot}15 \times 10^6}{55{\cdot}85n}\frac{7{\cdot}8}{3{\cdot}56} = \frac{3{\cdot}3 \times 10^6}{n},$$

which gives $I_0 = 1817$ when $n = 1$. Any other value of n greater than unity would make I much less than it is known to be from experiment *.

* Ashworth, "Magnetic and Electric Saturation Values," Phil. Mag., October 1918.

We may now proceed to consider certain relations which exist between the constants a', I_0, and R' amongst themselves and in connexion with the specific heat, both in the same and in different ferromagnetics.

5. *Relations of a' to R' and I_0 to θ.*

Equation (7) to the critical temperature for ferromagnetism discloses a simple and interesting relation between the maximum intensity of magnetization and the critical temperature. Writing the equation

$$\frac{\theta}{I_0} = \frac{8}{27}\frac{a'}{R'}, \quad \ldots \ldots \quad (16)$$

we find the ratio of $\frac{a'}{R'}$ is very approximately a whole number beginning with 2 for iron and increasing by successive units to 6 for magnetite. This is shown in Table I.

TABLE I.

Ferromagnetic.	$\frac{a'}{R'}$.	q.	Percentage difference from whole number.
Iron	7·0/3·56	2	+2
Cobalt	19·2/6·0	3	−6
Nickel	83·7/20·8	4	−0·6
Heusler's alloy	173/34	5	−1·7
Magnetite	203/35	6	+3

The departure from a whole number is largest with cobalt. There is some uncertainty in the values of the constants of cobalt, and the discrepancies here, and in what follows, are always larger with cobalt than with other ferromagnetics.

If we put

$$\frac{\theta}{I_0} = \frac{8}{27}q, \quad \ldots \ldots \quad (17)$$

q being $\frac{a'}{R'}$, then we may say that q has values which to a first approximation are whole numbers from 2 to 6, in consecutive order. There is apparently no ferromagnetic substance with $q=1$. If such should be found its critical temperature would probably be low unless the intensity of magnetization were very large.

The following table gives values of $\frac{\theta}{I_0}$ and the corresponding values of $q\frac{8}{27}$.

Table II.

Ferromagnetic.	$\frac{\theta}{T_0}$.	$q\frac{8}{27}$.	q.
Iron	0·58	0·59	2
Cobalt	0·95	0·89	3
Nickel.....	1·20	1·19	4
Heusler's alloy	1·50	1·48	5
Magnetite	1·79	1·78	6

The progressive increase by unit steps from 2 to 6 which q assumes from one to another of the ferromagnetics may be treated as an experimental fact apart from any theory, although it was first observed in connexion with the constants a' and R′ which are fundamental in the theory of ferromagnetism.

6. *Specific Heat and Ferromagnetism.*

The magnitude of the intrinsic field, $a'I^2$, of a magnet can be calculated when a' is known, and a' can be most easily determined from the equation to the critical temperature.

The maximum intrinsic field calculated in this way is of enormous magnitude regarded as a magnetic field, although it would be more correct to treat it as thermal rather than magnetic energy per unit of intensity of magnetization. With iron the intrinsic field at its maximum is $2{\cdot}31 \times 10^7$ gausses, and is as much as $4{\cdot}63 \times 10^7$ gausses with magnetite. At the critical temperature this enormous field vanishes, as the result of thermal action, and the energy associated with it which disappears is large enough to affect prominently the specific heat of the ferromagnetics at the critical temperature. Thus with nickel the specific heat at ordinary temperatures is about 0·109. It increases progressively up to 0·154, the true specific heat at the critical temperature (C_θ), and immediately above this temperature abruptly falls to 0·125, the discontinuity (Δc) of the specific heat being 0·029. The discontinuity is larger with other ferromagnetics, and is as much as 0·120 with iron. Weiss*, who has made careful and detailed experiments on this subject, treats the discontinuity of the specific heat as the equivalent of the loss of intrinsic magnetic energy which takes place when the temperature is raised to the critical point. According to the formula used by him, the intrinsic field is equal to NI, where N is a constant, and the magnetic

* P. Weiss and P. N. Beck, *J. de Phys.* (4) vii. p. 279 (1908).

energy associated with this field is then $\frac{1}{2}NI^2$. The calculation, even when revised and amended by H. A. Lorentz *, does not agree very well with experimental results, as will be seen in the table here given :—

TABLE III.

Ferromagnetic.	Δc. By Lorentz's formula [1].	Δc. By experiment.
Iron	0·089	0·120
Nickel.....	0·282	0·285
Magnetite	0·064	0·079

[1] Bulletin of the National Research Council, iii. pt. 3, no. 18, p. 123.

According to Lorentz, $\Delta c = \frac{4 \cdot 97}{m}$, where m is the molecular mass, and in order to arrive at the calculated result given above it is supposed that the magnetic carrier of iron is one atom, that of nickel three atoms, and that of magnetite $\frac{1}{3}(Fe_3O_4)$.

The discrepancy between calculation and experiment does not prove the connexion to be false between the intrinsic field energy and the discontinuity of the specific heat at the critical temperature ; it points rather to some defect in the formula which has been used in the calculation.

If, instead of the formula used by Weiss, we employ a formula in which the value of the intrinsic energy of magnetization is derived from the ferromagnetic equation, then it is possible to arrive at calculated results which are in very good agreement with the facts of experiment.

If the thermal energy of the discontinuity at the critical temperature, $\Delta c\theta$, is equated to the product of the maximum intrinsic field and the maximum intensity of magnetization, we get

$$f\Delta c\theta = a'I_0^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

f being a numerical factor. To express the thermal energy of the discontinuity in mechanical and in volume units we must multiply by J the mechanical equivalent of heat and by ρ the density. We have also to multiply by the factor n, which is the same in magnitude as in equation (15). We then have $f = nJ\rho$, and we get

$$n \,.\, \Delta c \,.\, \theta J\rho = a'I_0^3, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

* Lorentz, *Revue Scientifique*, 1912, p. 1.

from which we obtain the value of Δc, thus :

$$\Delta c = \frac{a' I_0^3}{n \rho J \theta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The truth of these equations is seen in the following table :—

TABLE IV.

Ferromagnetic.	n.	$n\Delta c\theta J\rho \times 10^{-10}$.	$a' I_0^3 \times 10^{-10}$.	Δc observed and used in the calculation.
Iron	1	4·26	4·20	0·120 (1)
Cobalt	1	4·75	5·52	0·098 (2)
Nickel	2	1·40	1·41	0·029 (3)
Heusler's alloy...	2	1·26	1·28	0·036 (4)
Magnetite.....	3/2	2·19	2·21	0·079 (5)

(1), (3), (5) Weiss, Piccard, and Carrard, *Arch. des Sc.* xlii. p. 378, and xliii. pp. 22, 113, and 199.
(2) A. Göbl, Thesis, Zurich University, 1911.
(4) Ashworth (unpublished).

Throughout the agreement is satisfactory, with the exception of cobalt.

In the equation which has been constructed we may replace $a' I_0^3$, by means of equation (14), with $\frac{27}{8} \frac{R\theta}{an} \rho$, and we get

$$n\Delta c J = \frac{27}{8} \frac{R}{an}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and writing $R' I_0^2/\rho$ for R/an, by equation (15), we obtain

$$n\Delta c J \rho = \frac{27}{8} R' I_0^2. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Either equation (21) or (22) allows Δc to be calculated, as all the other quantities are known by experiment with the exception of n, which may be obtained from (15) or (26).

We can put equation (21) thus :

$$\Delta c = \frac{27}{8} \frac{R}{J a n^2}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and since $\frac{27}{8} \frac{R}{J} = 6{\cdot}683$, we get

$$\Delta c = \frac{6{\cdot}683}{an^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

which applies to iron, cobalt, and nickel.

The calculation of Δc may be made from equation (22) instead of (21), and it is preferable to do so in the case of an alloy like Heusler's alloy and a compound such as magnetite, as the quantity $\rho R/an$ is replaced by the experimentally-determined product $R'I_0^2$, the reciprocal of Curie's constant and the intensity of magnetization, and this avoids a knowledge of a for the alloy and the chemical compound magnetite.

The following table gives the calculated and experimental values of Δc:—

TABLE V.

Ferromagnetic.	n.	Δc as $\frac{27}{8}\frac{R'I_0^2}{J\rho n}$.	Δc by experiment.	Percentage difference.
Iron	1	0·120	0·120[1]	± 0
Cobalt	1	0·114	0·098	+16
Nickel	2	0·029	0·029	± 0
Heusler's alloy ...	2	0·037	0·036	+ 2
Magnetite	3/2	0·079	0·079	± 0

[1] *Loc. cit.*

In the calculation there are no adjustable quantities, as n may be derived from other equations.

7. *Relation of Δc, the discontinuity, to C_θ, the specific heat, at the critical temperature.*

It has already been mentioned that a characteristic of ferromagnetic substances is the abnormal increase of the specific heat, which attains at the critical temperature very high values before the abrupt fall occurs which we have been considering. The specific heat C_θ at the critical temperature has the following values :—

Iron.	Cobalt.	Nickel.	Heusler's alloy.	Magnetite.
C_θ[1] = 0·309	0·270	0·154	0·179	0·299

[1] *Loc. cit., vide* Δc.

These are true specific heats, and they have been obtained by applying a correction to the mean specific heat between the critical temperature and a temperature of about 15° C. The values for iron and nickel have been determined with considerable precision, and are better known than the others.

These true specific heats have a simple relation to the discontinuity Δc. In general terms for elementary metals the relation may be expressed by the equation

$$maC_\theta = 5na\Delta c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

in which ma may be regarded as the molecular weight of the magnetic carriers much below the critical temperature and na the molecular weight just above the critical temperature. As m appears to have the value 2 for all the ferromagnetics when n has the numbers given above to it, and a is the same on both sides of the equation, we have

$$C_\theta = \frac{5}{2} n \Delta c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The verification of this is as follows :—

TABLE VI.

Ferromagnetic.	n.	$5\frac{n}{2}\Delta c$.	C_θ by experiment (1).	Percentage difference.
Iron.....	1	0·300	0·309	−3·0
Cobalt	1	0·245	0·270	−9·2
Nickel	2	0·145	0·154	−7·1
Heusler alloy	2	0·180	0·179	+0·5
Magnetite	3/2	0·296	0·299	−1·0

(1) *Loc. cit., vide* Δc.

Cobalt and nickel yield the least satisfactory results. Cobalt, according to A. Göbl, * has two discontinuities, one about 500° to 600° C., of magnitude 0·02, and the other at the critical temperature, of magnitude 0·098. It is the latter which appears in Tables IV. and V. If it is allowable to use the total discontinuity, which is 0·118, and to employ a corrected true specific heat at the critical temperature of 0·290, then cobalt has an error no larger than the other ferromagnetics. Thus in Tables IV. and V. the experimental and calculated values of Δc do not differ by more than 4 per cent., and in Table VI. C_θ, equal to 0·290, differs from the calculated value, 0·295, by less than 2 per cent.

With regard to nickel a very recent determination of C_θ and Δc by an electrical method puts $C_\theta = 0{\cdot}1577$ and $\Delta c = 0{\cdot}0325$, and the formula above would therefore give C_θ by calculation as 0·1625, with an error now of only +3 per cent. †

We can now obtain a formula for C_θ in terms of magnetic or thermal constants by substituting for Δc its equivalents. Thus we get

$$C_\theta = \frac{5}{2}\,\frac{27}{8}\,R'I_0^2\,\frac{1}{J\rho} \text{ in magnetic units} \quad . \quad . \quad (25)$$

* *Loc. cit.*, Table IV.

† Lapp, *C. R.* clxxxvi. pp. 1104–1106 (April 1928).

and $$C_\theta = \frac{5}{2}\frac{27}{8}\frac{R}{J}\frac{1}{na} \text{ in thermal units} \quad . \quad . \quad . \quad (26)$$

The latter reduces to

$$C_\theta = \frac{16{\cdot}79}{na}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

which applies satisfactorily to iron, cobalt and nickel, where a, the atomic weight, has a single definite value. With Heusler's alloy and magnetite we can substitute for R/aJ in the formula one-third of the specific heat at ordinary temperatures, in conformity with the law for pure metals that $3R/aJ$ is equal to the specific heat. Formulæ (23) and (26) may then be applied to Heusler's alloy and magnetite as with the other ferromagnetics.

8. (*a*) In all the formulæ where n appears it has, for any ferromagnetic, one and the same value, as may be seen in the tables given previously, and it means the number of atoms in the molecule above the critical temperature, that is, in the paramagnetic state.

The number of magnetic atoms in the molecule at ordinary temperatures in the ferromagnetic state is signified by m.

Now with nickel and Heusler's alloy n and m are alike, each being equal to 2, and therefore these metals show no change in the number of atoms to the molecule on passing through the critical temperature, but with iron and cobalt $m = 2$ and $n = 1$, and so in passing from the ferromagnetic to the paramagnetic state through the critical temperature there is a change in the constitution of the molecule, and the molecule of these metals becomes apparently monatomic in the paramagnetic condition.

(*b*) In the formula $maC_\theta = 5na\Delta c$ the number 5 is inserted arbitrarily, but it may be given a rational interpretation. The specific heat of a metal is by theory $3R/aJ$, in which R refers to the sum of the kinetic and potential energies for one degree of freedom. With metals generally there is an increase of specific heat with rise of temperature, which has been attributed to the progressive acquisition of rotational energy by the molecules, and this, in the case of the ferromagnetic metals, would be facilitated in virtue of the magnetic ties existing between the molecules. As these ties impose constraints to rotational motion, the energy acquired will be both potential and kinetic. The two degrees of rotational freedom thus added to the three degrees of translatory freedom give a total of five degrees of freedom, which would account for the number 5 in the formula.

At the critical temperature, the thermal agitation is assumed to be violent enough to rupture the magnetic or other molecular ties affecting rotation and, whilst the kinetic energy is preserved, the potential energy of rotations of two degrees of freedom vanishes, and its loss accounts for the discontinuity of the specific heat. If the potential and kinetic energies are equal, the discontinuity will be one-fifth of the whole specific heat, provided no change of molecular structure has taken place. With nickel and Heusler's alloy, in which there is no change in the molecule, Δc is very closely one-fifth of C_θ. Where there is a change from two atoms to one, Δc is two-fifths of C_θ.

(*c*) In a former paper (Phil. Mag. xlvii. p. 848, May 1924) reasons were given for considering the energy change on passing through the critical temperature as $\rho R\theta/an$, and this is not inconsistent with the values of the discontinuity of the specific heat if we understand R/an to apply to the equation,

$$\frac{\rho R\theta}{an} = \frac{8}{27} a' I_0^3,$$

whilst Δc applies to

$$J\rho n \Delta c \theta = a' I_0^3.$$

The first of these equations might be written

$$\frac{\rho R\theta}{an} = a'\left(\frac{2}{3} I_0\right)^3 = a'(I_0 - I_c)^3$$

since I_c, the critical intensity, is $\frac{1}{3} I_0$, and from this it appears that R/an refers to an energy change measured by loss of intensity of magnetization from I_0 to I_c, while Δc is measuring the whole loss of I_0.

9. *Ratios of the principal magnetic and thermal constants in groups of ferromagnetics.*

When the constants a', R', I_0, θ, Δc, and C_θ are compared in pairs of ferromagnetics, it is found that iron and nickel fall into one group and cobalt and magnetite fall into another group. A comparison of these groups is set out in Table VII.

Table VII.

		a'.	R'.	I_0.	θ.	Δc.	Increment of specific heat. $(C_\theta - C_{15})$	C_θ.
I.	Iron, Nickel	·085	·17	3·3	1·6	4·0	4·0	2·0
II.	Cobalt, Magnetite	·09	·17	3·0	1·6	1·25	1·25	0·9

Table of Fundamental Quantities and Constants.

	Iron.	Cobalt.	Nickel.	Heusler alloy.	Magnetite.
a ...	55·85	58·97	58·68	—	—
ρ ...	7·85	8·6	8·9	6·6	5·1
θ ...	1058° (1)	1349° (2)	661° (3)	633° (4)	853° (5)
I_0 ...	1817 (6)	1422 (7)	522 (8)	420 (9)	477 (10)
R' ...	3·56 (11)	6·0 (12)	20·8 (13)	34 (14)	35 (15)
a' ...	7·0	19·2	83·7	173	204
n ...	1	1	2	2	3/2
q ...	2	3·2	4	5	6
$\rho R/a$ ..	$11{\cdot}70\times10^6$	$12{\cdot}14\times10^6$	$12{\cdot}6\times10^6$	$10{\cdot}7\times10^6$	$11{\cdot}75\times10^6$
$R'I_0^2$ ..	$11{\cdot}76\times10^6$	$12{\cdot}13\times10^6$	$6{\cdot}34\times10^6$	$6{\cdot}00\times10^6$	$7{\cdot}67\times10^6$
R/aJ...	0·0356	0·0338	0·0339	(·116/3=·0387)	(·165/3=·055)
$a'I_0^3$ ...	$4{\cdot}197\times10^{10}$	$5{\cdot}52\times10^{10}$	$1{\cdot}41\times10^{10}$	$1{\cdot}28\times10^{10}$	$2{\cdot}21\times10^{10}$
Δc ...	0·120	0·098	0·029	0·036	0·079
$C\theta$ ...	0·309	0·270	0·154	0·179	0·299
C_{15} ...	0·112	0·107	0·109	0·116	0·165

(1) and (3) Ashworth, Phil. Mag., Jan. 1912.

(2) Stifler, Phys. Rev. ix p. 373 (1910).

(4) Ashworth.

(5) Weiss, Piccard, and Carrard, *Arch. des Sc.* xlii. p. 378 ; xliii. p. 22.

(6), (7), and (8) Ashworth, Phil. Mag. xxxvi. p. 351 (Oct. 1918).

(9) Ashworth (unpublished).

(10) Weiss, Piccard, and Carrard, *Arch. des Sc.* xlii. p. 378.

(11) Curie, ' Œuvres,' p. 227.

(12) Weiss and Bloch, *Arch. des Sc.* xxxiii. p. 293.

(13) Weiss and Foëx, *Arch. des Sc.* xxxi. pp. 5 and 89.

(14) Ashworth (unpublished).

(15) Weiss and Foëx, *Arch. des Sc.* xxxi. pp. 5 to 161.

A = Curie's constant.
J = Mechanical equivalent of heat = $4{\cdot}18\times10^7$.
R = Gas constant = $83{\cdot}2\times10^6$ ergs per degree C. for a gram molecule.
a = Atomic weight.
ρ = Density in grams per cubic centimetre.
θ = Critical temperature on the absolute scale.
I_0 = Maximum intensity of magnetization.
$R' = 1/kT$ = the reciprocal of Curie's constant.
a' = Intrinsic field constant = H/I^2.
n = Number of atoms in molecule above the critical temperature.
q = Ratio a'/R'.
Δc = Discontinuity of the specific heat.
$C\theta$ = True specific heat at the critical temperature.

Some of the correspondences observed in Table VII. must necessarily follow from the fact that the q values of iron and nickel have a ratio (2/4) the same as the q values of cobalt and magnetite (3/6). This applies to a' and R′ and to I_0 and θ. The explanation of the observed value of any one of these ratios is, however, obscure. Nevertheless it is clear that the several ferromagnetics are intimately related, and the meaning of these simple ratios will probably throw light on ferromagnetism and the structure of ferromagnetic bodies.

10. The table on p. 693 gives a list of some principal and useful quantities in ferromagnetism. Iron and nickel have been investigated more thoroughly than the other ferromagnetics, and the values given for their constants are probably not far from the truth; but with magnetite, and more particularly cobalt and Heusler's alloy, our knowledge of the constants is less precise. A complete revision of all would be of great use in the development of magnetic theory.

11. *Summary of Equations.*

I. $$\begin{cases} A = kT. \\ R' = 1/A. \end{cases}$$

II. $$R'I_0^2 = \rho R/an.$$

III. $$\begin{cases} (HI_0 + a'I_0I^2)\left(\dfrac{I_0}{I} - 1\right) = \dfrac{\rho RT}{an}. \\ \dfrac{\rho R_\theta}{an} = \dfrac{8}{27}a'I_0^3\,;\ I_c = \dfrac{I_0}{3};\ H_c = \dfrac{a'I_0^2}{27}. \end{cases}$$

IV. $$\theta/I_0 = \frac{8}{27}q\,;\ q = \frac{a'}{R'}.$$

V. $$\begin{cases} n\Delta c\theta J\rho = a'I_0^3. \\ n\Delta cJ = \dfrac{27}{8}R/an. \end{cases}$$

VI. $$C_\theta = \frac{5}{2}n\Delta c.$$

LXV. *A Note on Approximation Curves for a Fourier Series.* *By* H. V. Lowry, *The College of Technology, Manchester* *.

IF $S_n(x)$ is the sum of the first n terms of the Fourier series for $f(x)$, the curve $y=S_n(x)$ is usually called an "approximation curve," and it nearly coincides with $y=f(x)$, when n is large enough.

We can devise other functions which approximate to the Fourier series. The object of this paper is to show one such way of approximating to the series

$$2(\sin x-\tfrac{1}{2}\sin 2x+\tfrac{1}{3}\sin 3x-\ldots). \quad . \quad . \quad . \quad (1)$$

The method used also gives an insight into the origin of the discontinuities in the sum of this series.

When n is an integer

$$\sin^{2n}(\tfrac{1}{2}x)=\frac{2n!}{2^{2n-1}(n!)^2}\left\{1-\frac{n}{n+1}\cos x+\frac{n(n-1)}{(n+1)(n+2)}\cos 2x-\right.$$
$$\left.\ldots+(-1)^n\frac{n(n-1)\ldots1}{(n+1)\ldots2n}\cos nx\right\},$$

whence, integrating from 0 to x,

$$\int_0^x \sin^{2n}\tfrac{1}{2}u\,du=\frac{2n!}{2^{2n-1}(n!)^2}$$
$$\left\{x-\frac{n}{n+1}\sin x+\frac{n(n-1)}{(n+1)(n+2)}\frac{\sin 2x}{2}-\right.$$
$$\left.\ldots+(-1)^n\frac{n(n-1)\ldots1}{(n+1)\ldots2n}\frac{\sin nx}{n}\right\}.$$

This equation can be written

$$2\left[\frac{n}{n+1}\sin x-\frac{n(n-1)}{(n+1)(n+2)}\frac{\sin 2x}{2}\right.$$
$$\left.+\frac{n(n-1)(n-2)}{(n+1)(n+2)(n+3)}\frac{\sin 3x}{3}-\ldots\right]$$
$$=x-\frac{2^{2n}(n!)^2}{2n!}\int_0^x \sin^{2n}(\tfrac{1}{2}u)\,du. \quad (2)$$

When $n\to\infty$ the left-hand side of (2) approaches the

* Communicated by the Author.

series (1). Hence the behaviour of (1) can be deduced from the limiting form of the right-hand side of (2).

Now

$$\frac{2^{2n}(n!)^2}{2n!}\int_0^x \sin^{2n}(\tfrac{1}{2}u)du < \frac{2^{2n}(n!)^2 \sin^{2n}(\tfrac{1}{2}x)\pi}{2n!}, \quad . \quad (3)$$

when $0<x<\pi$; but, by Stirling's theorem,

$$\frac{2^{2n}(n!)^2}{2n!} = \sqrt{\pi n} \quad \text{nearly},$$

when n is large, and hence by (3)

$$\lim_{n\to\infty} \frac{2^{2n}(n!)^2}{2n!}\int_0^x \sin^{2n}(\tfrac{1}{2}u)du = 0,$$

provided $0<x<\pi$.

On the other hand, whatever the value of x,

$$\frac{2^{2n}(n!)^2}{2n!}\int_0^\pi \sin^{2n}(\tfrac{1}{2}u)du = \pi. \quad . \quad . \quad . \quad (4)$$

From (3) and (4) it follows that

$$\lim_{n\to\infty} \frac{2^{2n}(n!)^2}{2n!}\int_x^\pi \sin^{2n}(\tfrac{1}{2}u)du = \pi, \quad . \quad . \quad . \quad (5)$$

and by changing the variable to $2\pi-u$ we find that

$$\lim_{n\to\infty} \frac{2^{2n}(n!)^2}{2n!}\int_\pi^x \sin^{2n}(\tfrac{1}{2}u)du = \pi, \quad . \quad . \quad . \quad (6)$$

when $\pi<x<2\pi$, however near x is to π.

From (3), (5), and (6) we deduce that

$$\lim_{n\to\infty} \frac{2^{2n}(n!)^2}{2n!}\int_0^x \sin^{2n}(\tfrac{1}{2}u)du$$

$$= 0 \quad \text{when } 0<x<\pi,$$

$$= \pi \quad \text{when } x=\pi,$$

$$= 2\pi \quad \text{when } \pi<x<3\pi,$$

and generally

$$= 2r\pi \quad \text{when } (2r-1)\pi<x<(2r+1)\pi.$$

Therefore, when $n\to\infty$, (2) takes the form

$$2[\sin x - \tfrac{1}{2}\sin 2x + \tfrac{1}{3}\sin 3x - \ldots] = x - 2r\pi,$$

$$\text{when} \quad (2r-1)\pi<x<(2r+1)\pi.$$

Thus we have seen, in an elementary way, how the discontinuities arise in the Fourier series (1).

When n is large (3) is still very nearly true, and hence we may take

$$y = 2\left[\frac{n}{n+1}\sin x - \frac{n(n-1)}{(n+1)(n+2)}\frac{\sin 2x}{2} + \frac{n(n-1)(n-2)}{(n+1)(n+2)(n+3)}\frac{\sin 3x}{3} - \ldots\right] \quad (7)$$

as an approximating curve to the Fourier series.

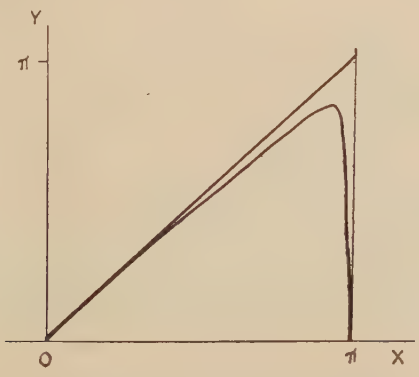
(2) shows that y is always less than x, when $0<x<\pi$, and hence there can be no Gibbs's phenomenon for such approximation curves. Moreover, by (2)

$$\frac{dy}{dx} = 1 - \frac{2^{2n}(n!)^2}{2n!}\sin^{2n}(\tfrac{1}{2}x),$$

whence we deduce that y has only one turning value, namely, a maximum, given by

$$\sin(\tfrac{1}{2}x) = \left(\frac{2n!}{2^{2n}(n!)^2}\right)^{\frac{1}{2n}} = \left(\frac{1}{\pi n}\right)^{\frac{1}{4n}} \quad \text{nearly,}$$

which is close to 1 for all values of n. Therefore y has a maximum value near $x=\pi$. Moreover, $\frac{d^2y}{dx^2}$ is negative for all values of x, and therefore gradient decreases continuously from $x=0$ to $x=\pi$. Therefore the general shape of the approximation curve (7) is



LXVI. *The Statistical Theory of Para- and Diamagnetism.* *By* Emrys Howells, *M.Sc.**.

THE foundations of the statistical theory of the magnetic properties of matter were laid by Langevin in 1905 †, and the main features of his work have permeated molecular theories since that time. The molecules were assumed to have orbital electrons which were equivalent to the molecular currents of Ampère and Weber and the consequent magnetism observed; this conception was applied by Langevin to the simple case of a gaseous medium.

One effect of the application of a magnetic field is the acceleration of the electrons in their orbits; diamagnetism is then ascribed to the resulting deformation of the electronic orbits, and the effect, being an affair of the internal constitution of the molecules, is practically independent of temperature. This occurs whether the molecules have a resultant magnetic moment or not.

When the molecular magnetic moments are not zero a paramagnetic effect is superimposed. Under the action of an applied magnetic field the molecules tend to orientate themselves in positions of lower potential energy—that is, with their axes in the direction of the field; this tendency is counteracted by the mutual collisions of the molecules which re-distribute the kinetic energy obtained from the field partly as kinetic energy of rotation and partly as kinetic energy of translation with a consequent conversion into heat. The condition of equilibrium is finally attained when the tendency to alignment with the field is balanced by the attempts of the collisions to turn the axes in all directions. The problem then yields to statistical treatment in the determination of the equilibrium distribution function and the calculation of the relation between the intensity of magnetization and the magnetic field.

It is clear that the problem reduces (on the basis of equipartition and classical statistics) to the determination of the distribution function for the final equilibrium state of magnetization; this analysis depends essentially on the assumptions made as to what is conserved during the collisions and interaction of the molecules. Langevin assumed that the molecules of a paramagnetic gas have equal and constant magnetic moments, and effects due to rotations about other

* Communicated by Prof. G. H. Livens.

† *Ann. de Chim. et Phys.* (8) v. p. 70 (1905).

axes together with intra-molecular forces were ignored, with the result that many experimental facts are not in accord with his form of the theory.

Among the attempts made to improve on Langevin's theory of para- and diamagnetism may be mentioned the work of Gans *, who assumed that substances are constituted of rigid axial magnetons which consist of negative electrons within a uniformly charged positive sphere. As pointed out by Livens †, the evaluation of the energy expression in the distribution formula, however, contains a series of errors which seriously influence his final results. This form of the theory, with certain modifications, can, however, be retained in seeking a generalization of the Langevin analysis to embrace both para- and diamagnetism.

We assume that the rotation of a molecule about an axis with angular momentum Ψ is equivalent to a magnetic moment $\mu\Psi$, where

$$\mu = \frac{e}{2mc} \text{ (electromagnetic units)}$$

is the equivalent magnetic moment of a single orbital electron having unit angular momentum, e being the electric charge on the electron measured in electromagnetic units, m its mass, and c the ratio of the electromagnetic measure of charge to the electrostatic ‡. If, then, we assume an axis of symmetry, and use the Eulerian coordinates (θ, ϕ, ψ) for the axes of principal inertia with corresponding moments A, A, C, the kinetic energy of the rotatory motions which are dynamically independent of the translatory motion is of the form

$$T = \tfrac{1}{2}[A(\dot{\theta}^2 + \sin^2\theta\dot{\psi}^2) + C(\dot{\psi} + \dot{\phi}\cos\theta)^2].$$

In addition, there is the magnetic potential energy, which, if the applied magnetic force B is along the polar axis of the coordinates, is

$$V = -\mu B[A\dot{\phi}\sin^2\theta + C\cos\theta(\dot{\psi} + \phi\cos\theta)],$$

the term in the square brackets representing the component of the resultant momentum in the direction of B.

According to the general theory, the distribution function defining the number of molecules with their space and

* Gans, *Ann. d. Phys.* xl. p. 149 (1916); l. p. 163 (1916).
† Livens, *Ann. d. Phys.* lxxv. p. 822 (1924).
‡ Livens, 'Theory of Electricity,' ed. 2, p. 391.

velocity coordinates in the usual differential range is $e^{-\frac{E}{R\vartheta}}$, where E is the total energy. In the Gans * analysis this is taken to be the sum of the kinetic and potential energies of the axial magneton ; this quantity, however, is not necessarily conserved on interaction of the molecules, and the correct expression must be sought in a more general way. In dynamical theory it is shown that for a general system defined by coordinates $q_1, q_2, \ldots . q_n$, the quantity

$$E = -L + \sum_{i=1}^{n} \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i$$

(where $L = T - V$) is such a function. When L involves the velocities q_i only as a homogeneous quadratic function the expression E reduces to $T + V$, but in other cases, as the present, where L contains terms linear in the velocities, no such reduction is possible. Then

$$L = \tfrac{1}{2}[A(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) + C(\dot{\psi} + \dot{\phi}\cos\theta)^2] + \mu B[A\dot{\phi}\sin^2\theta + C\cos\theta(\dot{\psi} + \dot{\phi}\cos\theta)],$$

and

$$E = \tfrac{1}{2}A(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2) + \tfrac{1}{2}C(\dot{\psi} + \dot{\phi}\cos\theta)^2.$$

The momenta are defined generally from the Lagrangian function L by the equations

$$\Theta = \frac{\partial L}{\partial \dot{\theta}} = A\dot{\theta},$$

$$\Phi = \frac{\partial L}{\partial \dot{\phi}} = A\sin^2\theta\dot{\phi} + C\cos\theta(\dot{\psi} + \dot{\phi}\cos\theta) + \mu B[A\sin^2\theta + C\cos\theta],$$

$$\Psi = \frac{\partial L}{\partial \dot{\psi}} = C(\dot{\psi} + \dot{\phi}\cos\theta) + \mu BC\cos\theta,$$

so that E can be written in the form

$$E = \frac{\Theta^2}{2A} + \frac{(\Phi - \Psi\cos\theta - \mu BA\sin^2\theta)^2}{2A\sin^2\theta} + \frac{(\Psi - \mu BC\cos\theta)^2}{2C}.$$

The number of elements per unit-volume for which the variables $\Theta, \Phi, \Psi, \theta, \phi, \psi$ lie within the differential range $d\Omega$ is

$$dn = ae^{-\frac{E}{R\vartheta}} d\Omega,$$

* Gans, *Ann. d. Phys.* xlix. p. 154 (1916); see also Lennard-Jones, Proc. Phys. Soc. xl. [5] (1928).

where

$$d\Omega = \sin\theta\, d\theta\, d\phi\, d\psi\, d\Theta\, d\Phi\, d\Psi.$$

The constant a is determined from the fact that the total number n of the molecules per unit-volume is specified, so that

$$n = a\int_{-\infty}^{\infty} e^{-\frac{E}{R\vartheta}} d\Omega.$$

Now each of the molecules in dn contributes to the magnetization along the direction of B an amount

$$\mu[A\dot{\theta}\sin^2\theta + C\cos\theta(\psi + \dot{\phi}\cos\theta)],$$

so that on the whole

$$I = a\mu\int_{-\infty}^{\infty} [A\dot{\phi}\sin^2\theta + C\cos\theta(\dot{\psi} + \phi\cos\theta)]e^{-\frac{E}{R\vartheta}} d\Omega,$$

$$= a\mu\int_{-\infty}^{\infty} [\Phi - \mu B(A\sin^2\theta + C\cos^2\theta)]e^{-\frac{E}{R\vartheta}} d\Omega,$$

$$= n\mu \frac{\int_{-\infty}^{\infty} [\Phi - \mu B(A\sin^2\theta + C\cos^2\theta)]e^{-\frac{E}{R\vartheta}} d\Omega}{\int_{-\infty}^{\infty} e^{-\frac{E}{R\vartheta}} d\Omega}$$

If, as assumed by Gans, the limits for Φ and Ψ are from $-\infty$ to $+\infty$ the integration yields a zero result—that is, if the range of variation of the motion in the rotatory coordinates is unrestricted, the resultant effect of the magnetic field is zero, no resultant polarity either of diamagnetic or paramagnetic character will be induced. If, then, a definite result is to be obtained, it is necessary to restrict the variation of at least one of the rotation momenta Φ and Ψ. It is difficult to say what limitations should be imposed, but in view of modern theories as to the structure of the atom, it is at least reasonable to suppose that Ψ is restricted to one or more definite constant values, the same for all molecules. We will first try one single value for Ψ, and also, as a further simplification and to make the expressions tractable, we shall assume that A is negligibly small ; for an electronic orbit this approximation is probably also justifiable, but in any case it enables us to obtain some idea of the form of the ultimate results.

Under these conditions we have then *

$$I = \frac{n\mu \int_0^{\pi} (\Psi - \mu BC\cos\theta) e^{-\frac{E}{R\vartheta}} \sin\theta\cos\theta\, d\theta}{\int_0^{\pi} e^{-\frac{E}{R\vartheta}} \sin\theta\, d\theta},$$

where

$$E = \frac{(\Psi - \mu BC\cos\theta)^2}{2C},$$

or, putting $x = \Psi - \mu BC\cos\theta$,

$$I = \frac{\int_{\Psi-\mu BC}^{\Psi+\mu BC} x(\Psi - x) e^{-\frac{x^2}{2RC\vartheta}} dx}{\int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx}$$

The polarization is therefore in part paramagnetic and in part diamagnetic, the former arising from the permanent angular momentum Ψ and the latter from the induced angular momentum $-\mu BC\cos\theta$. That these effects co-exist was pointed out by Gans †; the paramagnetism is caused by the thermal agitation of the molecules, so that the diamagnetism, which is an internal phenomenon, can predominate at sufficiently high temperatures. It is conceivable that in certain circumstances the two effects may just balance with the result that the medium appears to be non-magnetic.

Integration of the numerator leads to

$$I = \frac{nR\vartheta}{B} \frac{\left[\mu BC\left\{e^{-\frac{(\Psi+\mu BC)^2}{2RC\vartheta}} + e^{-\frac{(\Psi-\mu BC)^2}{2RC\vartheta}}\right\} - \int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx\right]}{\int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx}$$

$$= \frac{nR\vartheta}{B} \frac{\left[2\mu BC\, e^{-\frac{\Psi^2+\mu^2B^2C^2}{2RC\vartheta}} \cosh\frac{\mu B\Psi}{R\vartheta} - \int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx\right]}{\int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx}.$$

* These formulæ were given by Livens, 'Theory of Electricity,' ed. 2, pp. 393-394.

† *Gött. Nachr.* p. 197 (1910).

The complete integration gives difficulty, but under ordinary conditions of temperature and magnetic inducing force the numerator and denominator can be expanded, and only a few terms are required. The resultant magnetic intensity then becomes

$$I = \frac{n\mu^2\Psi^2 B}{3R\vartheta} - \frac{n\mu^2 CB}{3},$$

and susceptibility

$$\chi = \frac{n\mu^2\Psi^2}{3R\vartheta} - \frac{n\mu^2 C}{3}.$$

The first term represents the paramagnetism varying inversely as the absolute temperature in accordance with Curie's law *, which is well verified for paramagnetic gases and is in good agreement with observations for certain paramagnetic solutions and for some solid salts.

The second term stands for the diamagnetism, which, as expected, is independent of the temperature. Generally speaking the two types will be present; the one or the other will predominate according to temperature—a rise in temperature being favourable to diamagnetism.

The condition for a resultant diamagnetic effect is

$$\frac{\Psi^2}{C} < R\vartheta,$$

or

$$\tfrac{1}{2}C\omega^2 < \tfrac{1}{2}R\vartheta,$$

where ω is the angular velocity of a molecule about its axis. In other words, the kinetic energy of the rotatory motion of a molecule must be less than the energy of translation. If the particular temperature at which this change of magnetism is observed for a substance, an estimate of $\frac{\Psi^2}{C}$ can be made.

The first term in the magnetic intensity is the outcome of the view that paramagnetism arises from the effort of the magnetic field to orientate the molecules which are spinning about as the result of gaseous encounters. If, therefore, the whole of the internal energy of the medium associated with its magnetization is to be regarded as added thermal energy, then Curie's law is a natural result,

$$\chi = \frac{\Delta}{\vartheta}.$$

* Curie, *Ann. de Chim. et Phys.* (7) v. pp. 289-405 (1895); see also Auerbach, 'Modern Magnetics,' ch. viii.–ix.

If only the proportion $\frac{\vartheta}{\vartheta+\Delta}$ of the internal energy is converted into heat, we shall have a modified law of the form

$$\chi = \frac{\Delta}{\vartheta + \mathrm{K}}.$$

There are a number of substances, including paramagnetic solids, which obey this form of variation with temperature *.

The Internal Field.

In the case of a gas the mutual magnetic influence of the neighbouring molecules can be neglected, but when the molecules are very close together, as in a solid body, the local interaction field may assume large proportions †. The nature of the field is unknown ; it is not necessarily electric or magnetic in character, but progress is not impossible.

It is evident that we cannot deal with the highly irregular field of the individual molecules, and therefore we take an average estimate of this variable magnitude, which is regarded as constant over the physically small element of volume on account of the enormous number of molecules contained in it.

Weiss postulates that, on an average, the molecular field is proportional to the intensity of magnetization, so that the complete magnetic force is

$$\mathrm{B} + \alpha \mathrm{I}.$$

Following Weiss, we can obtain a theory for solid bodies by substituting this complete value instead of B in the general expression which still retains its form. In particular, if there is no applied magnetic inducing force, $\mathrm{B} = 0$, and we have, if $\mathrm{I}_s = n\mu\Psi$,

$$\mathrm{I} = \frac{\mathrm{I}_s\left[\frac{n\mathrm{R}\vartheta}{\alpha \mathrm{II}_s}\left\{2\mu\mathrm{C}\alpha\mathrm{I}e^{-\frac{1}{2\mathrm{RC}\vartheta}\left(\frac{\mathrm{I}s^2}{\mu^2n^2}+\mu^2\alpha^2\mathrm{I}^2\mathrm{C}^2\right)}\cosh\frac{\alpha \mathrm{II}_s}{n\mathrm{R}\vartheta} - \int_{\frac{\mathrm{I}_s}{\mu n}-\mu\mathrm{C}\alpha\mathrm{I}}^{\frac{\mathrm{I}_s}{\mu n}+\mu\mathrm{C}\alpha\mathrm{I}} e^{-\frac{x^2}{2\mathrm{RC}\vartheta}}dx\right]}{\int_{\frac{\mathrm{I}_s}{\mu n}-\mu\mathrm{C}\alpha\mathrm{I}}^{\frac{\mathrm{I}_s}{\mu n}+\mu\mathrm{C}\alpha\mathrm{I}} e^{-\frac{x^2}{2\mathrm{RC}\vartheta}}dx}.$$

Besides‡ the zero solution, $\mathrm{I} = 0$, there is another solution,

* Livens, 'Theory of Electricity,' Appendix i.; See also Weiss, *Journal d. Phys.* (4) vi. p. 661 (1907).

† Bull. Nat. Research Council, iii. pt. 3 (1922); Heisenberg, *Zeit. für Phys.* xlix. p. 619 (1928).

‡ Livens, 'Theory of Electricity,' ed. 2, p. 400; see also Peddie, 'Molecular Magnetism, chap. iv.

and this accounts for permanent magnetization. Moreover, this non-zero solution, when it exists, represents the stable condition of the medium, because the magnetic potential energy in it is a medium. The zero solution corresponds to a maximum value of the potential energy, and is therefore in general unstable.

At ordinary temperatures the approximate form is sufficiently accurate even for high values of the magnetic field. This gives

$$I = \frac{\alpha I_s^2 I}{3nR\vartheta},$$

and indicates a limiting temperature,

$$\vartheta_s = \frac{\alpha I_s^2}{3nR},$$

at which spontaneous magnetization becomes possible. If we introduce this critical temperature into the relation

$$I = \frac{I_s^2(B+\alpha I)}{3nR\vartheta}$$

we have

$$I = \frac{B\vartheta_s}{\alpha(\vartheta - \vartheta_s)}.$$

This is Weiss's modification of the Curie law already mentioned; the expression retains its form, but the temperature is now measured from the critical point ϑ_s. Many substances obey the modified law, and determinations of α have been made*. Values of the order 10^6 absolute units have been obtained, so that it is not surprising that the intensity of magnetization does not sometimes appear to be affected by the external applied field.

Low Temperature Considerations.

The investigation of the magnetic behaviour of substances at low temperatures has caused considerable difficulty both experimentally and theoretically. It is now of interest to examine how far the present theory, based on classical statistical mechanics, can account for the peculiar deviations from the simple linear laws.

* Stoner, 'Magnetism and Atomic Structure,' chap. iv.; *vide* Bull. Nat. Res. Council, p. 119.

The general expression for the magnetic intensity can be written

$$I = nR\vartheta \frac{\partial}{\partial B} \log \left\{ \frac{1}{\mu BC} \int_{\Psi-\mu BC}^{\Psi+\mu BC} e^{-\frac{x^2}{2RC\vartheta}} dx \right\}$$

$$= nR\vartheta \frac{\partial}{\partial B} \log \left[2e^{-\frac{\Psi^2}{2RC\vartheta}} \left\{ 1 + \frac{\mu^2 B^2 C^2}{3!} \left(\frac{\Psi^2}{R^2C^2\vartheta^2} - \frac{1}{RC\vartheta} \right) \right.\right.$$

$$\left.\left. + \frac{\mu^4 B^4 C^4}{5!} \left(\frac{\Psi^4}{R^4C^4\vartheta^4} - \frac{6\Psi^2}{R^3C^3\vartheta^3} + \frac{3}{R^2C^2\vartheta^2} \right) + \ldots \right\} \right],$$

giving

$$\frac{I}{n\mu\Psi} = \left(\frac{\mu\Psi B}{3R\vartheta} - \frac{\mu CB}{3\Psi} \right) - \left(\frac{\mu^3\Psi^3B^3}{45R^3\vartheta^3} + \frac{4\mu^3\Psi CB^3}{45R^2\vartheta^2} - \frac{2\mu^3B^3C^2}{45R\vartheta\Psi} \right) + \ldots$$

Taking $\mu = \frac{e}{2mC} = \cdot 89.10^7$ electromagnetic units, and for the magnetic moment *

$$\mu\Psi = 3\cdot 6.10^{-21},$$

we have for the angular momentum

$$\Psi = 4.10^{-28}.$$

Moreover, if $B = 10^3$ gauss,

R = Boltzmann's gas constant for single molecule,

$= 1\cdot 36.10^{-16}$ erg per degree,

moment of inertia $C = 10^{-41}$ gram cm.^{2},

$$\vartheta = 300^\circ,$$

we have, for order of terms,

$$\frac{I}{n\mu\Psi} = (10^{-5}) - (10^{-11}) + \text{smaller quantities.}$$

Under ordinary conditions the first bracket is sufficient; it is clear that fall of temperature to (say) 10° will not demonstrate any material variation from the usual law The additional terms will not assert themselves until ϑ is below 1°. Variations, however, are known to occur at 70° for some substances. To explain this it is necessary to assume that the extra terms hitherto neglected become large by a

* These values are taken from the work of Reiche, Von Weyssenhoff, and Oosterhuis, Bull. Nat. Res. Council, pp. 101-102.

substantial increase in the force B, which is here taken quite generally to include any local field, if necessary ; this is not an unreasonable assumption, as powerful intra-molecular fields are known to exist and must be expected to become effective in the regions of temperature where the molecules come much closer together, finally leading to the domination of crystal structure.

If, for example, we insert the value 10^6 for B, which is of the order determined experimentally by Oxley and others *,

$$\frac{I}{n\mu\Psi} = (0{\cdot}029 - 0{\cdot}074) - (0{\cdot}01),$$

the modifying term being negative. In the graph of $\frac{n\mu\Psi}{I}$

Fig. 1.

against ϑ this would indicate a deviation from the straight line. This term may also be positive ; in fact, it is at first at very low temperatures positive, and becomes negative with decreasing temperature. The positive deviation is shown in fig. 1.

This is followed by the opposite deviation, shown in the lower part of fig. 2.

If the new term gains supremacy there arises the possibility of maximum and minimum positions indicated in fig. 3. At the very lowest temperatures the temperature factor $e^{-\frac{x^2}{2RC\vartheta}}$ in the integrals becomes exceedingly small, and the

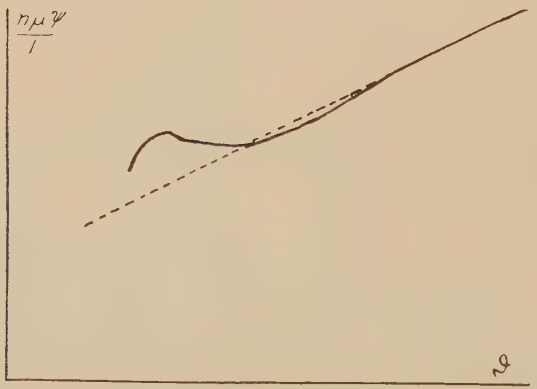
* *Journ. d. Phys.* (4) vi. p. 661 (1907) ; Stoner, 'Magnetism and Atomic Structure,' chap. iv.

integration gives the saturation value $n\mu\Psi$. This accounts for the result that the intensity becomes practically independent of temperature just above absolute zero.

An extensive series of experiments has been conducted by Jackson * on paramagnetism at low temperatures. A few

Fig. 2.

Fig. 3.



substances obey the Curie law down to the lowest temperatures; others conform to Weiss's modification of the same law, still retaining the linear relationship. However, it was found that deviations occur. Considering double sulphates, a curve similar to that of fig. 1 was obtained, the intensity

* Phil. Trans. A, cciv. pp. 1-48 (1923).

increasing more rapidly with fall of temperature than is indicated by the linear law. The effect was considerable in the case of cobalt ammonium sulphate, less with nickel ammonium sulphate, and too small for measurement with ferrous ammonium sulphate. Jackson also obtained the cryomagnetic effect illustrated by the lower portion of the curve in fig. 2; in this case the intensity increases less rapidly with fall in temperature than is demanded by the usual relation. Certain salts also exhibited a maximum or minimum at the lowest temperatures.

We have succeeded in showing the character of the deviations by postulating a large local field: the magnitude of the effects depends on the strength of the field and on how it grows and gains dominance with falling temperature. The increasing field and decreasing temperature assist in magnifying the effects as we proceed down the temperature scale.

Quantum Modifications.

It may be objected that the analysis is based on classical equipartition ideas; according to Planck's First Quantum Theory the mean energy of an oscillator of frequency ν is

$$\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{R\vartheta}} - 1},$$

where $h = 6{\cdot}558.10^{-27}$ erg-secs. (Planck's constant). At ordinary temperatures the expansion of the expression gives $R\vartheta$, but at low temperatures this is inaccurate. Since the new value is smaller than $R\vartheta$, the introduction of Planck's form simply serves to increase the deviations (particularly at the lower part of the scale) without affecting their character. The saturation point would be reached sooner, and complete magnetic saturation would prevail over a certain range of temperature.

On the classical theory the law of distribution is a continuous one, and integration is taken over all values. According to the orientation law of quantization only certain positions are possible. If θ is the angle between the direction of the effective moment of the magnet and the field B, the values are determined by

$$\cos\theta = \frac{1}{m}, \frac{2}{m}, \frac{3}{m}, \frac{4}{m}, \ldots \frac{m}{m},$$

where m is an integer.

Acting on this assumption the general expression becomes

$$I = nR\vartheta \frac{\partial}{\partial B} \log \Sigma e^{-\frac{(\Psi - \mu BC\cos\theta)^2}{2RC\vartheta}}$$

or *

$$I = nR\vartheta \frac{\partial}{\partial B} \log \Sigma_1^n e^{-\frac{\Psi^2}{2RC\vartheta} + \frac{\mu B\Psi}{R\vartheta}\binom{P}{m} - \frac{B^2C}{2R\vartheta}\binom{P}{m}^2}.$$

If $m = 1$,

$$\frac{I}{n\mu\Psi} = 1 - \frac{\mu BC}{\Psi}.$$

Since $\cos\theta = 1$, all the axes are orientated parallel to the field direction, and we expect the saturation value indicated. If $m = \infty, \ldots . -\infty$,

$$\frac{I}{I_s} = -\frac{\mu BC}{3\Psi} + \frac{\mu B\Psi}{3R\vartheta}.$$

If we therefore regard the saturation value obtained for the case $m = 1$ as what we expect at absolute zero, and the other value as the result for usual conditions, it seems that the restricting forces accounting for the quantized positions lose their power as the temperature rises, this being a parallel to the classical theory.

If it is assumed that the molecules can have other momenta values which are integral multiples of Ψ, it is found that the additional terms due to the factors $e^{-\frac{2\Psi^2}{RC\vartheta}}, e^{-\frac{9\Psi^2}{2RC\vartheta}}, e^{-\frac{8\Psi^2}{RC\vartheta}}, \ldots .$ are negligible. From this it appears that when higher values are ascribed to the angular momenta the dominating terms are those corresponding to the smaller values, and the tendency to increase the magnetic intensity is almost negligible. The reason for this lies in the character of the distribution function—there being less tendency to alignment with the field direction under these conditions.

Summary and Conclusion.

A generalization of Langevin's statistical theory of magnetization is developed somewhat on the lines laid down by Gans by assuming that the magnetization of the molecules arises from their angular motions and is influenced by the magnetic force. By making certain simple assumptions and developing the theory on classical lines it proves to be more

* *Vide* R. H. Fowler, 'Statistical Mechanics,' chap. xii.

than adequate enough for giving a general description of the trend of magnetization. The paramagnetism appears as the Curie term, varying inversely with absolute temperature, and is the outcome of the permanent molecular angular momentum. The diamagnetism is constant, being independent of the temperature, and is ascribed to the induced angular momentum. With the introduction of a molecular field permanent magnetization is accounted for.

Even at low temperatures, where its failure is most to be expected, the theory succeeds in demonstrating the character of the typical deviations. On introducing a large local field the peculiarities become more pronounced and resemble those observed experimentally below 70°.

The effect of substituting Planck's function $f(\mathrm{R}\mathfrak{H})$ for $\mathrm{R}\mathfrak{H}$ is to magnify the deviations, and indicates the probability of saturation over a range of temperature just above absolute zero; this is borne out by empirical evidence.

Quantum orientation corresponds to the general classical result for $m = \infty$ and to the saturation value of zero temperature for $m = 1$, indicating greater freedom from restricting forces with rise of temperature.

The problem seems to turn about the term

$$\frac{\mu\Psi\mathrm{B}}{f(\mathrm{R}\mathfrak{H})},$$

powers of which play an important rôle at low temperature and with strong fields. It becomes necessary to have a further knowledge of how and when the intra-molecular forces assert themselves with falling temperature, and this involves an acquaintance with the structural form of the medium.

LXVII. *Some Series in the Extreme Ultra-Violet Spark Spectra of Copper.* *By* F. C. Chalklin, *Ph.D., University of Sheffield* *.

§1. It has been found by Prof. O. W. Richardson and the writer † that many of the numerous critical potentials found for iron, cobalt, nickel, and copper in the soft X-ray region could be arranged in series of the type

* Communicated by Prof. O. W. Richardson, F.R.S.

† Proc. Roy. Soc. A, cxix. p. 64 (1928); cxxi. p. 218 (1928).

$A-\frac{b}{n^2}$. More recently the writer * has found that some of his results for manganese could be treated in the same way.

The series scheme appears to be capable of extension to cover the low voltage effects found by Thomas † for iron, cobalt, nickel, and copper, using the same value of b as in the higher voltage series of the element concerned, but choosing a new value of A.

For copper, using the original value of b, 2360, and choosing for A the value 39·7 volts, the results given in Table I. are obtained. To conform with the previous notation, the initial energy level A has been called X_4.

Table I.

$b=2360$, $X_4=39{\cdot}7$ volts.

n.	9.	10.	11.	12.	13.
$X-\frac{b}{n^2}$	10·6	16·1	20·2	23·3	25·7
Experimental value...	$\overline{10{\cdot}3}$	15·7	20·7	23·8	25·5

Values with a bar have also been used elsewhere.

The agreement shown between experimental results and the values from the series is quite good. The experimental effects obtained by Thomas at 12·3, 14·2, and 19·0 volts are left unexplained, but, apart from these, we are now able to account for all the discontinuities up to 40 volts. (The critical potentials at 33·7 and 35·5 volts are probably unresolved higher members of the series.)

Table II.

n.	9.	10.	11.	12.	13.
$X_4-\frac{b}{n^2}$	13·9	19·6	23·8	27·0	29·5
Experimental break..	14·1	19·4	24·3	—	28·8

The weakness of this series lies in the smallness of the number of terms. The same difficulty applies to the corresponding series for iron, cobalt, and nickel. For these elements the series are further weakened by the absence of the critical potential for $n=12$. We venture to give this doubtful series for iron in Table II., firstly because it seems

* Phil. Mag. ix. p. 847 (1930).

† Phys. Rev. xxv. p. 322 (1925); xxvi. p. 744 (1925).

to correspond to the more secure series just given for copper, and, secondly, because of the completeness with which the series scheme, thus extended, explains the critical potentials given by Thomas for iron. We find that, for this element, 36 out of 45 of Thomas's discontinuities are explained on the basis of the series scheme, with the same value of "b" employed throughout. The value of X_4 chosen is 43·8 volts, and the value of b used in all the iron series is 2420. Corresponding series can be applied to the low voltage effects for cobalt and nickel, with $X_4=40{\cdot}3$ and 41·3 volts respectively, and with $b=$ 2357 volts in each case.

§ 2. Returning to the more secure series for copper, it is observed that it extends over a spectral region examined by Millikan and Bowen* in their ultra-violet spark experiments. It is of obvious importance to discover whether or not the series suggested to account for the critical potentials have their counterpart in the spectroscopic work. The conditions are very different in the two types of experiment; in the former case the critical potentials are observed as a result of the excitation of radiations from a solid under electronic bombardment, and, in the second case, the spectral lines are excited in a probably ionized vapour by a spark discharge. It would, therefore, be surprising if we were to find identical series in the two cases, and a similarity is all that we can hope for. In the event of such a similarity being found, it will suggest that there is some common factor in the two modes of excitation.

It is found, however, that the Millikan results contain a series very nearly identical with the critical potential series. Using the series formula $A_1-\frac{b}{n^2}$ and putting $A_1=39{\cdot}62$ volts as compared with $A=39{\cdot}7$ volts in the critical potential case, and giving to b the value 2395, instead of 2360, we obtain the values shown in Table III.

In the table, and in succeeding tables, I have taken the liberty of changing Millikan and Bowen's wave-lengths into volts by the formula $V=\frac{12345}{\lambda}$. The series starts apparently for $n=10$, but the line for $n=9$ would be

* Phys. Rev. xxiii. p. 1 (1924).

outside the Millikan region. The term $n=9$ is later shown to be present. The writer proposes to defer the discussion of the intensities until later in the paper. It is necessary to make sure that the apparent agreement between the lines and the series formula is not due to the lines being so close together that an agreement was bound to occur. We find that, between 700 and 600 Å., the average distance apart of lines is ·15 volt; between 600 and 500 Å., ·20 volt; between 500 and 400 Å., ·25 volt; and between 400 and 300 Å., ·40 volt. In Series 1 the greatest error was ·03 volt for the line 484·5 Å., *i.e.*, in a region where the average distance apart of lines is ·25 volt. From this standpoint the series seems to be satisfactory. The writer

Table III.—Series 1.

$A_1=39{\cdot}62$ volts; $b=2395{\cdot}1$.

n.	10.	11.	12.	13.	14.	15.
$A_1-\frac{b}{n^2}$ (volts)	15·67	19·83	22·99	25·45	27·40	28·98
Millikan & Bowen (volts)	15·66	19·81	23·00	25·48	27·40	28·97
λ in Å.	788·3	623·1	536·8	484·5	450·5	426·1
Intensity	6	0	0	4	2	1
Estimated intensity...	5	3	2	2	1	1

has found no mention of the probable error in the measurement of the spectral lines, but, in a previous paper, Millikan, Bowen, and Sawyer * say "wave-lengths accurate to about ·2 Å."

An attempt was next made to see if there were more series of this type capable of fitting the copper data. It was found that there was another series employing the same final level but involving a new system of initial levels. These were again of the form $\frac{b}{n^2}$ and involved a value of b equal to 230·14 volts.

Whilst there are only five lines in series 2, it must be borne in mind that in choosing the series formula, only the value of b was arbitrary. The numerical agreement is decidedly good. No line appears for $n=4$.

* Astrophysical Journal, liii. p. 150 (1921).

The value of b (230·14) corresponds to an effective nucleus of 4·13e.

As there are now two sets of $\frac{b}{n^2}$ terms, we will differentiate between them by calling those for which $b=2395{\cdot}1$, $\alpha(n)$, and those for which $b=230{\cdot}14$, $\beta(n)$.

It is found that there are lines corresponding to transitions from the $\beta(n)$ terms to $\alpha(10)$. These combination lines are given in Table V.

TABLE IV.—Series 2.

$A_1=39{\cdot}62$. $b=230{\cdot}14$ volts.

n.	5.	6.	7.	8.	9.
$A-\frac{b}{n^2}$	30·41	33·23	34·92	36·02	36·78
Millikan & Bowen (volts).	30·41	33·24	34·91	36·03	36·76
λ in Å.	405·9	371·4	353·6	342·6	335·8
Intensity	2	2	1	3	4
Estimated intensity	3	2	1	1	0

TABLE V.—Series 3.

n.	5.	6.	7.	8.	9.
$\alpha(10)-\beta(n)$ from series...	14·74	17·56	19·25	20·35	21·11
$\alpha(10)-\beta(n)$ from actual lines.	14·75	17·58	19·25	20·37	21·10
Millikan & Bowen (volts)	14·77	17·63	19·22	20·37	21·12
λ in Å.	836·0	700·1	642·3	606·0	584·6
Intensity	2	3	0	1	1
Estimated intensity ...	3	2	1	1	0

Row 2 has been obtained by taking $\frac{2395{\cdot}1}{10^2}-\frac{230{\cdot}14}{n^2}$.

Row 3 is obtained by subtracting the actual line $A_1-\alpha(10)$ from the line $A_1-\beta(n)$. It is to be noted that in these combinations three errors are involved; an error in each of the lines or terms from which the combination is calculated and an error in the line with which comparison is made. In the circumstances the agreement seems to be good, and greatly strengthens the scheme. The range of Millikan and Bowen's work has only allowed the $\alpha(n)$

terms to be extended down to $n=10$. If a term of this type exists for $n=9$, then we should expect to find transitions $\alpha(9)-\beta(n)$. These transitions are found. We get $\alpha(9)=\frac{2395\cdot1}{n^2}=29\cdot57$ volts. Since $A_1-\alpha(9)=39\cdot62-29\cdot57=10\cdot05$ volts, the combination lines should be 10·05 volts less than the corresponding $A_1-\beta(n)$ lines. This method has been employed in the second row of Table VI.; the first row is calculated from $\frac{2395\cdot1}{9^2}-\frac{230\cdot14}{n^2}$.

Table VI.—Series 4.

n.	5.	6.	7.	8.	9.
$\alpha(9)-\beta(n)$ Calculated ...	20·36	23·18	24·87	25·97	26·73
$\alpha(9)-\beta(n)$ Using actual line to get β (n).	20·36	23·19	24·86	25·98	26·71
Millikan line in volts ...	20·37	23·21	24·84	25·92	26·59
Millikan line in Å. ...	606·0	531·8	496·9	476·2	464·3
Intensity	1	0	3	3	5
Estimated intensity ...	3	2	1	1	0

Table VII.—Series 5.

$A_2=53\cdot71$ volts.

n.	11.	12.	13.	14.	15.
$A_2-\frac{b}{n^2}$	33·92	37·08	39·54	41·49	43·07
Millikan & Bower (volts)	33·91	37·05	39·51	41·54	43·09
λ in Å.	364·0	333·2	312·4	297·2	286·5
Intensity	2	4	1	0	0
Estimated intensity ...	4	3	2	2	1

The first three terms agree well with our expectations, and the fourth fairly well, but the fifth seems to be too far out. Once again, however, we may regard this combination series as solidifying the scheme that we have built up.

There are no combination lines for $\alpha(8)$ and it may be taken that this term is not present. Similarly there are no combinations for $\alpha(11)$.

It is found that there is another series of lines employing the $\alpha(n)$ terms and a new final level A_2. This series is given in Table VII. and seems to fit reasonably well.

Again, the $\alpha(n)$ terms may be employed with another final level A_3 at 38.335 volts to give another series of Millikan lines. These are shown in Table VIII.

TABLE VIII.—Series 6.

$A_3 = 38{\cdot}335$ volts.

n.	10.	11.	12.	13.	14.	15.	16.	17.
$A_3 - \frac{b}{n^2}$	14·39	18·54	21·70	—	26·12	27·69	28·98	30·04
Millikan & Bowen (volts).	14·39	18·52	21·73	—	26·13	27·64	28·97	30·03
λ in Å.	858·1	666·4	568·1	—	472·5	466·6	426·1	411·2
Intensity	2	1	0	—	3	4	1	0
Estimated intensity	6	4	3	2	2	1	1	0

It is observed that the line for $n = 13$ is missing. This will receive explanation when the intensities are dealt with.

There appear to be no lines indicating transitions from the $\beta(n)$ terms to the A_3 level given by Series 6, until the terms for $n = 7$ is reached. From $n = 7$ to $n = 10$ we find lines with the correct wave-length for transitions of this type. These are shown in Table IX. Until the A_3 level

TABLE IX.—Series 7.

n.	7.	8.	9.	10.
$A_3 - \beta(n)$	33·64	34·74	35·49	36·03
Millikan & Bowen (volts) ...	33·64	34·75	35·45	36·03
λ in Å.	367·0	355·3	348·2	342·6
Intensity	1	1	3	3
Estimated intensity	2	1	1	0

was found, none of the series obtained showed an overlapping of $\alpha(n)$ and $\beta(n)$ terms; the $\alpha(n)$ terms failed beyond $n = 15$, at a depth of 10·64 volts, whilst the $\beta(n)$ terms started at $n = 5$, at a depth of 9·21 volts. In Series 6, however, in dealing with the transitions to the A_3 level, it was found that the $\alpha(n)$ terms persisted up to $n = 17$, at a depth of 8·29 volts, and so it is rather interesting that the $\beta(n)$ terms giving transitions to the A_3 level do not start until $\beta(n) = 7$, at a depth of 4·70 volts.

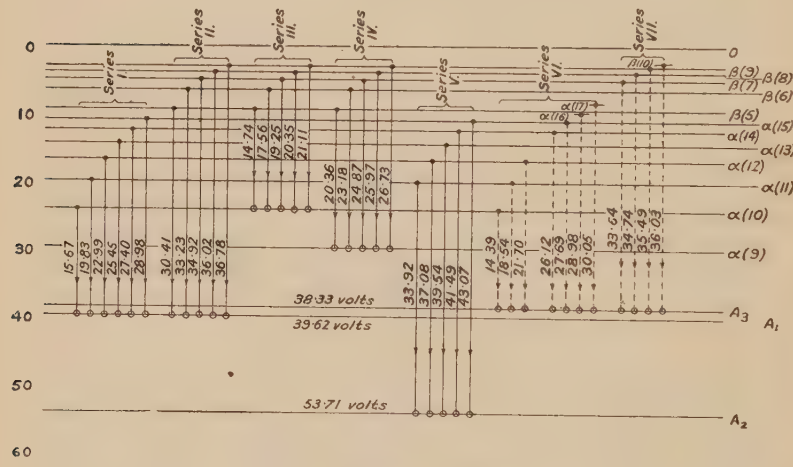
Hence, if the series involving A_3 are regarded apart from the previous series, the $\alpha(n)$ and $\beta(n)$ terms never overlap.

The energy levels involved in the series are represented in fig. 1. The arrows indicate the experimental results of Millikan and Bowen. The diagram shows that the series scheme fits together rather well.

§ 3. *Intensities.*

In the tables giving the series, the fourth row gives the intensities found by Millikan and Bowen. It is at once seen that they are not at all what one would expect for

Fig. 1.



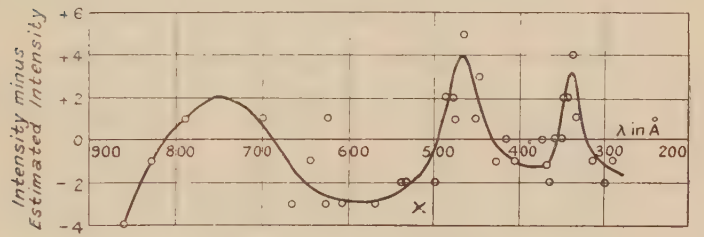
Energy diagram for Copper.

genuine series. This was regarded as a very serious difficulty. If the peculiar arrangement of intensities in the series were due to actual differences in the probabilities of the initital levels, then it would be expected that, in comparing two series originating in the same set of initial levels, we should find a similar arrangement of intensities. We do not find this.

It is, however, to be expected that the intensities will depend to some extent on the experimental conditions and it is also to be expected that the intensities may be modified by uneven sensitiveness of the photographic plate. If this be the case, then it will be found that in a sensitive region

all the lines will be stronger than their position in the series scheme would lead one to expect, and in an insensitive region all the lines should be too weak. Assuming the series scheme to be true, the intensity to be expected for each line was estimated. Subtracting this value from the actual intensity obtained by Millikan and Bowen, the error due to the photographic sensitiveness and other causes should be obtained. This should be a function of the wave-length, and hence, if we plot it against the latter, a curve should be obtained. Such a curve is shown in fig. 2. With one exception (possibly due to two lines being coincident) every point falls reasonably well on a smooth curve. Moreover, it is seen that peaks appear—peaks very suggestive of the absorption bands found in the optical region. From X-ray data it is found that bromine

Fig. 2.



is predicted to have an N_7 edge at 410 Å., and an $N_{5,6}$ edge at 1100 Å., whilst silver should have an $N_{5,6}$ absorption edge at 280 Å.* Going in the direction of shorter wave-lengths, Thoraeus's † measurements predict the bromine $M_{1,2}$ edge at 175 Å., and the other M levels will occur at still shorter wave-lengths. The determination of the edges from the X-ray data is not likely to be very accurate in this long wave-length region. It is to be perceived, however, that absorption edges are to be expected in the neighbourhood of the wave-lengths at which we have found intensity peaks, and that the description of the sensitiveness of the plate is a reasonable one.

In Series 6 it was observed that the line $A_3-\alpha(13)$ was missing. This is explained by the sensitiveness curve, for the line would be expected at a little under 510 Å. and

* Taken from A. H. Compton's 'X-Rays and Electrons,' p. 190.
† Phil. Mag. ii. p. 1015 (1926).

would be in a region of low sensitiveness. The line is indicated by a cross in fig. 2.

Only a small fraction of the lines tabulated by Millikan and Bowen has so far been dealt with, and it is not improbable that the scheme is capable of considerable extension. In these circumstances it seems inadvisable to advance any theory to account for the phenomena dealt with. We have therefore contented ourselves with summarising the salient features arising from the series classification.

(1) Just as Rydberg series can be fitted to the critical potentials of soft X-ray excitation for iron, nickel, cobalt, manganese, and copper, so can series of the same type be fitted to the vacuum spark lines of copper.

(2) The A_1 level for the spectra agrees exactly with the X_4 level for the critical potentials. Of the two values for "b" occurring in the $\frac{b}{n^2}$ terms, one, at 2395·1, is very close to the critical potential value at 2360.

(3) The scheme so far embraces three arbitrary final levels, A_1, A_2 and A_3, and two sets of levels of the form $\frac{b}{n_2}$, described as $\alpha(n)$ and $\beta(n)$.

(4) The A_1 level has transitions from both the $\alpha(n)$ and the $\beta(n)$ levels. The A_2 level only receives transitions from the $\alpha(n)$ levels. A_3 receives jumps from the $\alpha(n)$ levels and also from the $\beta(n)$ levels. There are transitions from the $\beta(n)$ levels to the $\alpha(n)$ levels.

(5) The effective nucleus involved in the $\alpha(n)$ terms is $13{\cdot}3e$. This corresponds to the critical potential value of $13{\cdot}2e$. The effective nucleus for the $\beta(n)$ terms is $4{\cdot}13e$.

(6) The intensities of the lines lead to a reasonable curve for the sensitiveness of the photographic plate as a function of the wave-length.

Points (1) and (2) give rise to the suggestion that there is, in those portions which emit radiations between 300 Å.

and 1000 Å., something in common between the excitation of the copper in Millikan and Bowen's vacuum sparks and the excitation of solid copper by electronic bombardment in the soft X-ray experiments. It may be, therefore, that a more complete analysis of the Millikan lines will throw light on the problem of the origin of the numerous critical potentials found for solids in the soft X-ray region, thus giving information on the state of the periphery of the atom in solids.

Recently Ericson and Edlén* have published a brief account of some experiments on copper using a vacuum spectrograph designed by Siegbahn, with a considerably greater dispersion than that of Millikan and Bowen. Their published plates extend from a little over 100 Å. to 550 Å., and they obtain far more lines than did Millikan and Bowen. Ericson and Edlén have not yet published their numerical results, but, from a study of their photographs, these are not expected to invalidate our series.

In conclusion, the writer would like to express his gratitude to Prof. O. W. Richardson for his kind interest and advice.

LXVIII. *The Effect of Temperature on the Viscosity of Air.* *By* W. G. Shilling, *M.C., D.Sc., and* A. E. Laxton, *M.Sc., A.I.C.*†

THE experiments described below were undertaken as a result of Rankine's criticism‡ of Williams's measurements§ on the effect of temperature on the viscosity of air from room-temperature up to 1000° C. Some of the objections raised have already been answered by Williams‖. Since this work was completed ¶, Edwards ** has completed a series of experiments, the results of which do not agree with those obtained by Williams.

* Nature, cxxiv. p. 688 (1929); *Zeits. für Physik*, lix. p. 665 (1930).
† Communicated by the Authors.
‡ Proc. Roy. Soc. A, cxi. p. 219 (1927).
§ *Loc. cit.* cx. p. 141 (1926).
‖ *Loc. cit.* cxiii. p. 233 (1927).
¶ *Loc. cit.* cxvii. p. 245 (1928).
** In the summer of 1927.

In principle the method is exactly that used by Williams. Modifications have been introduced where necessary to ensure that the doubts raised by Rankine's criticisms should be covered.

The first serious criticism raised concerns the temperature measurements in Williams's work, with particular reference to the fact that only one thermoelement was used for the whole of the temperature measurements. Our experience with a method of heating such as that used by Williams is that the central portion of the furnace is extremely uniform in temperature and is very easily controlled. Moreover, the efficient lagging permissible and the constancy of heat supply enable the temperature to be maintained to $\pm 1^\circ$ C. for several hours. In addition, the central portion of the furnace containing the preheating bulb and spiral was shut off by fire-clay stoppers, thus enabling conditions approximating to black-body radiation to be maintained, especially at the higher temperatures used. One thermocouple will then presumably give the correct temperature reading for the whole of the enclosure. To test this point, five thermocouples were used throughout the present work. The furnace used by Williams was again employed. One thermocouple, No. 5, was placed exactly as in Williams's experiments. The other four were evenly distributed, with their hot junctions near the capillary and placed as shown in the subsidiary sketch of fig. 1. Their positions longitudinally are shown in the main diagram. Each thermocouple was separately calibrated using the fixed points employed by Williams, and, in addition, were checked from 700° C. upwards by a disappearing filament type of pyrometer reading to $\pm 1^\circ$ C. The cold junctions of Nos. 1 to 4 were immersed in a water-box placed near the furnace and fed from a tap with cold water. For No. 5 thermocouple the cold junction was immersed in the thermostat. The cold-junction corrections were made by means of the experimentally-determined equation

$$y = 6{\cdot}16t - 8{\cdot}6,$$

where y is the number of microvolts correction to be applied and t is the temperature of the cold junction in degrees centigrade. Table I. shows the type of result obtained. The figures give the temperature of each thermocouple for a definite furnace temperature.

Readings in Table I. are taken to the nearest 0·5° C., the limit to which the higher temperatures could be taken with certainty.

From Table I. it can be seen that had the temperatures been measured only by No. 5 thermocouple little difference would be made. It is doubtful whether the vapour-bath method of heating, used by Edwards, has any advantage over an electric furnace for such work. The temperatures obtainable by vapour baths are limited both in range and in number.

TABLE I.

Comparison of Thermocouple Readings.

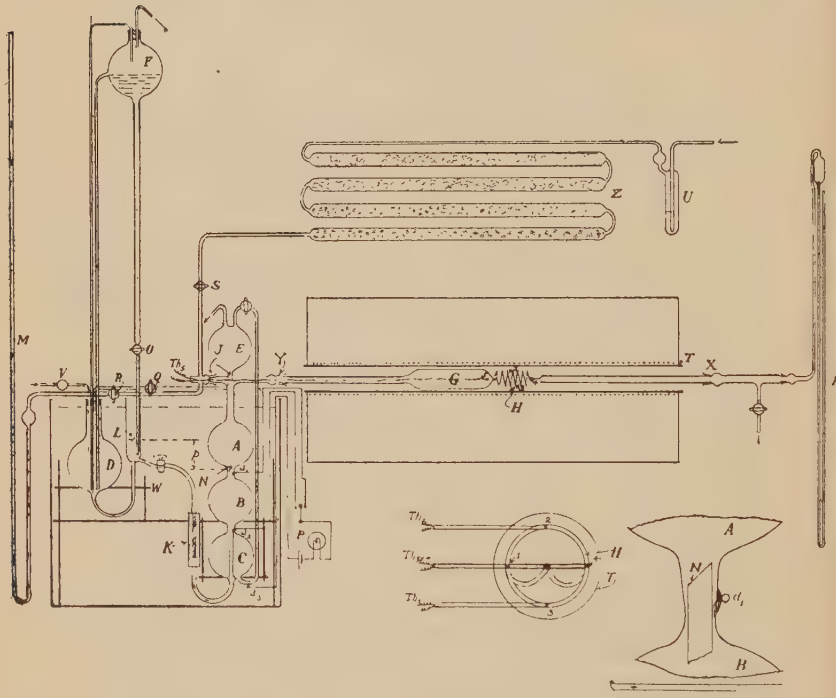
Thermocouple.				Mean 1–4.	5.	Mean temp.
1.	2.	3.	4.			
123·5	124·5	124·0	124·0	124·0	124·0	124·0
124·0	124·0	123·0	124·5	124·0	124·5	124·0
181·5	182·5	182·0	182·0	182·0	181·5	182·0
189·5	188·5	189·0	188·5	189·0	189·5	189·0
258·0	258·5	257·5	258·0	258·0	257·5	258·0
359·0	359·5	358·5	358·5	359·0	359·0	359·0
431·5	430·5	431·0	431·0	431·5	430·0	431·0
537·5	537·0	536·5	536·5	537·0	538·0	537·0
699·5	700·0	700·5	701·5	701·0	700·0	701·0
847·0	847·5	846·5	847·5	847·0	847·0	847·0

The principal modification of Williams's apparatus was was made as a result of the next point raised by Rankine, namely, the pressure control.

This criticism has already been fully answered by Williams. To remove any possibility of error caused by personal fatigue, the pressure feed shown in fig. 1 was designed to be automatic when once started. Each of the bulbs A, B, and C has a capacity of about 300 c.c. At the commencement of an experiment the tube leading from C up to E is filled with mercury, and a little mercury remains in C. The latter bulb has the same function as the first bulb in Williams's apparatus. It is of sufficient size to ensure equilibrium by the time the mercury has risen to the point d_2, which is the beginning of the calibrated

volume between the points d_1 and d_2. The subsidiary sketch in fig. 1 shows the form of the top contact d_1 and also the end of the tube N. The bottom contact d_2 is similar. The bulb A is inserted to steady the flow and to ensure that the volume of the gas leaving B is at the measured thermostat temperature. From A the gas goes directly into the furnace to the preheater G.

Fig. 1.



The remainder of the apparatus shown in the thermostat is the device for feeding mercury into the bulbs at constant pressure. An overflow head L is fixed at a height indicated by p above the overflow tube N, which terminates between the bulbs A and B. The overflow L is fed by a stream of mercury controlled by a sensitive tap O from the flask F, secured by stout brackets to the wall at a little more than barometric height vertically above L. The flask F is kept filled to the overflow side-tube from the flask D by means of suction and a con-

trolled air-inlet V. The overflow from L returns to the flask D. It was found necessary to maintain a constant level in F, otherwise the stream flowing into L gradually diminished, giving a slight decrease in the driving pressure due to lowering of the meniscus at L. Also the stands holding the apparatus had to be constructed of stout L-iron, rigidly connected, with the feet firmly placed on a thick base. If rigidity is not thus ensured, the transfer of about 700 c.c. of mercury from one side of the stand to the other during an experiment caused changes of pressure amounting to as much as 0·1 mm. of mercury.

The main platform of the stand carried bulb B, which rested in a carefully-shaped cup cut in a crossbar of teak. The four corner posts of the stand were of $\frac{3}{4}$ in. diameter brass rod, and passed through heavy adjusting collars fixed to the platform. The height of each platform was adjustable. The weight in bulb C was supported by a teak stand slung from the main platform. Two of the corner posts were extended so that clamps could be affixed to support the glass apparatus above bulbs A and D respectively.

The height of the bulb D is adjustable relative to bulbs A, B, and C. Connexion is made by a length of glass tubing inside a piece of rubber pressure-tubing as shown at K. This connecting piece could be made of any convenient length, thus enabling the driving pressure to be varied. The height of stand W could be separately adjusted to suit the pressure required.

By applying suction at E, the mercury filling bulbs B and C at the end of each experiment could be raised into E by opening the stopcock connecting C to E.

Then, by opening the stopcock Q, the mercury was allowed to run back by gravity into D ready for the next experiment.

The mercury was periodically withdrawn from bulb E for cleaning, although most of the oxide collected in the bulbs D and F, and gave no trouble in the experimental bulbs C or B. As the mercury left the bulbs B and C, fresh gas was allowed to enter through the purifying train by opening the stopcock S. The stopcock R, connecting the oil manometer M, was closed during this process to avoid undue disturbance of the oil-levels. Until bulb C was about one-third full in the next experiment the stopcock R was not reopened. The working of this apparatus was

extremely smooth and the pressure very constant throughout the longest experiments. Deviations from the mean pressure never exceeded 0·5 mm. pressure of oil having a density given by

$$d^{t^\circ\,\mathrm{C.}}_{4^\circ\,\mathrm{C.}} = 0{\cdot}9072 - 0{\cdot}00064t.$$

This equation was determined experimentally for the oil used.

The remaining criticism raised by Rankine concerns the calibration and testing of the capillary used. For our experiments The Thermal Syndicate, Ltd., kindly sent us a selection of tubes to be calibrated throughout their length. Calibration was done by the mercury-pellet method, and the tubes were rotated at each point so that their mean diameters at angles of 60° could be estimated, thus checking uniformity of cross-section. The best tube for our purpose had a bore of about 0·4 mm. and a length of 100 cm. The maximum difference in bore did not exceed 10 per cent. of the bore, and deviations were much less than this over the greater part of the length. All cross-sections seemed to be perfectly circular, although, unless the tube is broken, these measurements are admittedly difficult to make. The calibrated tube was then returned to the makers, who undertook to coil it into a spiral without any risk of flattening of cross-section. The resulting spiral had six turns with a pitch of 8 mm. and an outside diameter of 5·2 cm. Great care was taken to avoid any sudden bends, especially near the ends. The whole of the transpiratory apparatus was of transparent silica. The spiral was connected directly to the preheating vessel C on one side and to a length of 1·3 cm. bore tubing terminating in half of a ground joint X on the other. Connexion of the glass apparatus to the preheater was made by a further length of wide tubing reaching out of the furnace and also terminating in half of a ground joint Y. The other half of this joint was of ordinary soda glass for direct connexion to the top of bulb A. The dimensions of the preheater (6·4 cm. diameter and 19·5 cm. long) were proved sufficient by the fact that no variation was observed in the temperature recorded by thermocouple No. 5 when the first rush of gas took place in each experiment before equilibrium was reached in filling the bulb C.

The final test of the suitability of the capillary was then made. Experiments were made with the driving pressures

roughly in the ratios 1 : 2 : 3, all other conditions remaining the same. If Meyer's formula holds, the time taken will be inversely proportional to the pressure used. The suggestion made by Rankine that this test should be made on Williams's capillary could not be carried out, since the

TABLE II.

p_1-p_2 dynes/cm.^{2}	p_2 dynes/cm.^{2}	V_1 c.c.	t_1° C.	$\eta_1\times10^4$.	τ_1.	$\kappa(1+4\xi_1/R)\times10^{10}$.
36,710	1,014,100	286·90	22·9	1·8235	1833·6	3·9558
36,600	1,014,300	286·90	22·9	1·8235	1847·4	3·9370
36,400	1,017,700	287·29	23·3	1·8255	1852·6	3·9140
36,530	1,018,100	287·29	23·3	1·8255	1851·2	3·9461
36,570	1,014,700	286·90	22·9	1·8235	1848·2	3·9205
36,620	1,014,500	287·00	23·0	1·8240	1849·0	3·9340
36,740	1,013,900	287·44	23·45	1·8262	1837·6	3·9566
36,670	1,017,100	286·90	22·9	1·8235	1842·0	3·9407
				Mean		3·9380

TABLE III.

p_1-p_2 dynes/cm.^{2}	p_2 dynes/cm.^{2}	V_1 c.c.	t_1° C.	$\eta_1\times10^4$.	τ_1.	$\kappa(1+4\xi_1/R)\times10^{10}$.
71,800	1,015,200	287·29	23·3	1·8255	955·2	3·9539
72,010	1,015,200	286·81	22·8	1·8230	952·8	3·9407
72,140	1,015,200	287·19	23·2	1·8250	955·2	3·9334
71,450	1,015,200	287·23	23·24	1·8252	960·0	3·9511
71,720	1,015,200	286·90	22·9	1·8235	955·0	3·9487
71,900	1,015,200	286·56	22·55	1·8218	950·8	3·9488
72,070	1,022,300	287·27	23·28	1·8254	956·0	3·9345
71,940	1,022,100	286·90	22·9	1·8235	950·0	3·9575
				Mean		3·9461

tube was unfortunately broken by workmen during a summer vacation. But, in spite of the difficult nature of the work, all the capillaries sent us by The Thermal Syndicate compared well with the best glass capillaries

available. The results of the tests on the capillary are set out in Tables II. to IV. below, the symbols used in these and in subsequent tables having the same meaning as in the corresponding tables in Williams's communication. The last column of each table gives the capillary constant uncorrected for slip. The values found for this constant under different driving pressures show that Meyer's formula holds to the limits of experimental error.

Table IV.

p_1-p_2 dynes/cm.^{2}	p_2 dynes/cm.^{2}	V_1 c.c.	$t_1°$ C.	$\eta_1\times10^4$.	τ_1.	$\kappa(1+4\xi_1/R)\times10^{10}$.
107,780	1,005,100	288·90	24·3	1·8304	655·0	3·9357
107,970	1,005,200	287·63	23·65	1·8271	650·8	3·9303
108,130	1,005,200	287·29	23·3	1·8255	649·0	3·9275
108,130	1,005,100	287·10	23·1	1·8245	647·0	3·9347
108,040	1,005,000	286·61	22·6	1·8221	647·0	3·9262
108,020	1,005,200	286·71	22·7	1·8225	645·6	3·9375
107,930	1,005,400	286·90	22·9	1·8235	647·2	3·9360
107,760	1,006,600	286·90	22·9	1·8235	648·2	3·9257
107,780	1,006,600	287·15	23·15	1·8247	646·4	3·9424
				Mean		3·9329

The results of Tables II. to IV. are conveniently summarized in Table V.:—

Table V.

Driving pressure (dynes/cm.^{2}).	Mean value of $\kappa(1+4\xi_1/R)\times10^{10}$.
36,600	3·9380
72,000	3·9461
108,000	3·9329
Mean value	3·9390

From the mean value of $\kappa(1+4\xi_1/R)\times10^{10}$ the true value of κ, corrected for slip, was calculated exactly as described by Williams. Using the values $\kappa=0{\cdot}0_93939$ (Table V.) and L=100 cm., the value of R is 0·02116 cm.

The corrected values of κ and R are $0{\cdot}0_9 3932$ and 0·02115 cm. respectively.

Since the lower half of Williams's temperature range seems to be more open to criticism than the upper half, particular attention was paid to the region below 200° C. Measurements were then made at higher temperatures up to 850° C., at which point the work had to be discontinued.

Gas volumes at the temperature of each experiment were calculated from the calibrated volume of bulb B and the known pressure at 23° C. by using Berthelot's Equation of State. The critical pressure for air was taken as 39·3 atm., and a value of 132·6° abs. was used for the critical temperature. For the main series of experiments the highest of the three calibration pressures, namely ca. 108,000 dynes/cm.^{2}, was used as being the most convenient. The air was purified by the train of reagent tubes shown in fig. 1. The rate of flow was indicated by the wash-bottle U, containing sulphuric acid, which also served to dry the air. From this wash-bottle the air passed through a tube containing broken stick potassium hydroxide to remove carbon dioxide, a tube of calcium chloride for the initial drying, followed by two tubes containing phosphorus pentoxide. All these tubes were of liberal dimensions. Before commencing experiments the whole apparatus was tested under a pressure of 1 mm. of mercury by evacuating at the end normally forming the gas-exit. No leakage greater than that corresponding to a rise in pressure of 1 mm. on standing overnight was tolerated. To obviate any possibility of back-pressure the manometer and fittings were removed at X for all experiments.

The calibrated volume of bulb B between the contact points d_1 and d_2 was 287·0 c.c. at 23° C. All times were measured to $\pm 0{\cdot}2$ sec. by an accurate stop-watch, the daily rate of which was checked against wireless time-signals. Times of experiments varied from 650 sec. at room-temperature to 6000 sec. at the highest temperature measured.

In Table VI. are given the experimental results. Table VII. gives the experimental values of η with the corresponding values of $T^{3/2}/\eta$.

When the values of $T^{3/2}/\eta$ are plotted against temperature the resulting line is almost straight, but shows a

TABLE VI.

p_3-p_4 dynes/cm.^{2}	p_4 dynes/cm.^{2}	V_2.	τ_2.	t_2° C.	$\frac{\eta_2\times10^4}{1+4\xi_2/R}$.
107,070	1,007,500	331·68	832·6	69	2·0146
107,290	1,007,200	332·65	834·2	70	2·0138
107,340	1,006,800	332·65	834·8	70	2·0164
107,440	1,001,900	383·13	1068·0	122	2·2415
107,420	1,001,800	385·08	1069·2	124	2·2375
107,060	1,002,500	385·08	1075·4	124	2·2380
107,220	1,003,100	385·08	1074·8	124	2·2421
107,910	1,005,400	441·36	1376·8	182	2·5193
107,970	1,005,800	443·30	1368·6	184	2·4945
107,660	1,006,100	447·18	1371·0	188	2·4705
107,770	1,005,100	448·15	1367·8	189	2·4615
107,590	1,007,600	513·16	1742·0	256	2·7339
107,640	1,007,900	515·10	1748·8	258	2·7353
108,030	1,008,400	514·13	1756·0	257	2·7615
107,760	1,008,700	518·98	1777·4	262	2·7623
107,220	1,011,400	615·01	2371·6	361	3·0959
107,590	1,011,400	613·07	2348·4	359	3·0855
107,800	1,010,800	607·25	2344·6	359	3·0861
107,940	1,010,600	613·07	2344·8	359	3·0901
108,100	1,000,500	683·71	2802·6	430	3·3136
107,900	992,100	684·84	2829·6	433	3·3328
107,600	999,700	684·84	2838·4	433	3·3270
108,080	992,600	684·84	2826·2	433	3·3355
108,320	1,005,500	776·01	3429·0	527	3·5813
107,730	1,005,600	773·10	3455·0	524	3·6032
107,480	1,007,400	780·86	3504·6	532	3·6107
108,060	1,007,900	785·71	3508·8	537	3·6116
107,540	1,012,500	844·87	3980·0	598	3·7929
107,990	1,011,000	844·87	3970·0	598	3·7982
108,300	1,008,100	942·83	4711·4	699	4·0498
107,640	1,007,700	944·77	4764·4	701	4·0629
108,240	1,006,500	929·25	4616·8	685	4·0241
107,690	1,008,400	1009·7	5327·2	768	4·2527
107,650	1,007,600	1013·6	5325·0	772	4·2329
108,180	1,015,100	1067·9	5792·2	828	4·4025
107,660	1,014,900	1086·4	5979·2	847	4·4516

TABLE VII.

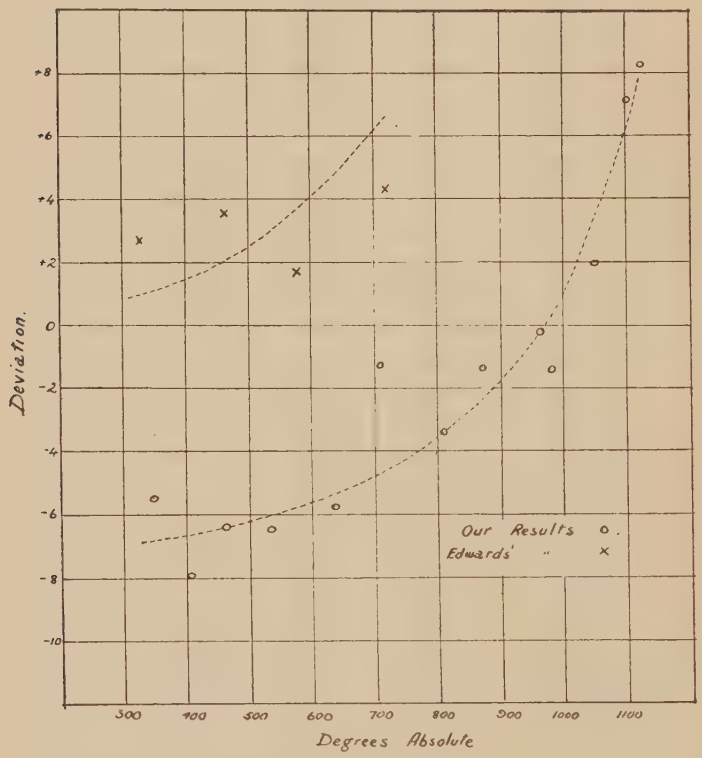
Experimental Results.

Temp. ° C.	Temp. ° abs.	$\eta_2 \times 10^4$.	$T^{3,2}/\eta \times 10^{-7}$.
69	342	2·019	3·140
70	343	2·018	3·148
70	343	2·021	3·144
122	395	2·247	3·494
124	397	2·243	3·527
124	397	2·243	3·527
124	397	2·247	3·520
182	455	2·527	3·841
184	457	2·502	3·905
188	461	2·478	3·995
189	462	2·469	4·023
256	529	2·743	4·435
257	530	2·771	4·403
258	531	2·745	4·458
262	535	2·772	4·464
359	632	3·099	5·127
359	632	3·099	5·127
359	632	3·103	5·120
361	634	3·109	5·135
430	703	3·330	5·598
433	706	3·349	5·601
433	706	3·343	5·611
433	706	3·352	5·597
524	797	3·623	6·210
527	800	3·601	6·284
532	805	3·631	6·291
537	810	3·632	6·348
598	871	3·816	6·736
598	871	3·821	6·727
685	958	4·051	7·319
699	972	4·078	7·432
701	974	4·091	7·431
768	1041	4·284	7·840
772	1045	4·264	7·922
828	1101	4·438	8·233
847	1120	4·488	8·353

distinct tendency to curve. On the assumption that this curvature might be due to experimental errors, a straight line was drawn as nearly as possible through the results. The intercept with the temperature axis gave a numerical value of 116 for the Sutherland Constant.

Using this value for the constant, the actual divergences from the "true" value were plotted from the

Fig. 2.



results given in Table VII. The "true" value is that calculated for the temperature in question on the assumption that Sutherland's law is obeyed. The four values obtained by Edwards* were similarly treated, using his experimental value for the constant, viz., C = 118. In fig. 2 the divergences from the "true" values are shown as parts per thousand on the true value of η. The trend of

* *Loc. cit.*

these experimental errors (indicated by the broken lines) both in the case of our own work and in that of Edwards, indicates that there is a small but steady deviation from Sutherland's law over the temperature range observed.

There is no indication of the sudden break which Williams obtained by joining his results on to those of other workers at the low temperature end. The experimental method used by Williams is considered to be completely vindicated against all criticism made against it by Rankine. It is suggested that the peculiar results which Williams found were due to his method of smoothing his experimental results.

After this work was completed, a publication by Braune, Basch, and Wentzel * gives results supporting the above conclusions. In addition, they agree † with some of Williams's replies to Rankine's criticisms.

Summary.

1. The coefficient of viscosity of air has been measured by the comparative transpiration method over the temperature range 23°–850° C. Particular attention has been paid to points raised in criticisms of Williams's work, and the method which he used has been completely vindicated.

2. The results show that there is a small but steady deviation from Sutherland's law over the range considered.

3. It is suggested that the peculiar results obtained by Williams are due to his method of smoothing experimental values.

In conclusion, the authors desire to thank Prof. J. R. Partington, M.B.E., D.Sc., for his interest and helpful suggestions throughout the course of the work. They wish also to thank the Department of Scientific and Industrial Research and the London County Council for maintenance grants. Thanks are also due to the Chemical Society for a grant which defrayed part of the cost of the apparatus.

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* *Z. Phys. Chem.* cxxxvii. p. 176 (1928).
† *Ibid.* p. 187.

LXIX. *The Multistage Valve Amplifier.* *By* A. C. Bartlett, *B.A.* (Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley.)

Summary.

The nth power of a second order square matrix is first obtained, and then from this the equations of the multistage amplifier.

1. *Preliminary.*

If I_1 is the current flowing into the input terminals of a passive four-terminal network, I_2 is the current flowing from the output terminals, while V_1 and V_2 are the voltages across the input and output respectively, then it is known that

$$V_1 = aV_2 + bI_2,$$
$$I_1 = cV_2 + dI_2,$$
where $$(ad - bc) = 1,$$

and a, b, c, and d are constants depending on the particular structure of the network.

Thus V_1 and I_1 are obtained from V_2 and I_2 by a homogeneous linear substitution, of which the matrix is

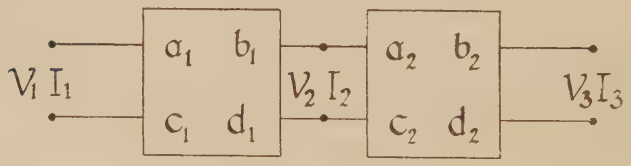
$$\begin{vmatrix} a, & b \\ c, & d \end{vmatrix},$$

of which the determinant

$$ad - bc = 1.$$

If there are two networks, as in fig. 1, of which the

Fig. 1.



matrices are

$$\begin{vmatrix} a_1, & b_1 \\ c_1, & d_1 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} a_2, & b_2 \\ c_2, & d_2 \end{vmatrix},$$

then

$$V_2 = a_2 V_3 + b_2 I_3,$$
$$I_2 = c_2 V_3 + d_2 I_3,$$
$$V_1 = a_1 V_2 + b_1 I_2,$$
$$I_1 = c_1 V_2 + d_1 I_2.$$

Thus V_1 and I_1 are obtained from V_3 and I_3 by the successive application of the two substitutions *. Therefore V_1 and I_1 are obtained from V_3 and I_3 by a linear substitution, of which the matrix is

$$\begin{vmatrix} a_1, & b_1 \\ c_1, & d_1 \end{vmatrix} \times \begin{vmatrix} a_2, & b_2 \\ c_2, & d_2 \end{vmatrix} = \begin{vmatrix} a_1a_2 + b_1c_2, & a_1b_2 + b_1d_2 \\ c_1a_2 + d_1c_2, & c_1b_2 + d_1d_2 \end{vmatrix}.$$

This process can be continued for a chain of any number of networks, the matrix of the substitution for the whole chain being the product in order of the matrices of the constituents. In particular, if the chain consists of n successive identical members, the matrix of the whole chain is the nth power of the matrix of one element. A network having a pair of output and a pair of input terminals may be specified by three constants, Z, θ, and ϕ †, and then the equations relating V_1 and I_1 with V_2 and I_2 are

$$V_1 = \frac{\cosh(\theta+\phi)}{\cosh\phi} \cdot V_2 + \frac{Z \sinh\theta}{\cosh\phi} \cdot I_2,$$

$$I_1 = \frac{\sinh\theta}{Z\cosh\phi} \cdot V_2 + \frac{\cosh(\theta-\phi)}{\cosh\phi} \cdot I_2.$$

But it is also known that if there is a chain of n identical networks, and if V_1 and I_1 are the input volts and current, and V_{n+1} and I_{n+1} are the output volts and currents, then

$$V_1 = \frac{\cosh(n\theta+\phi)}{\cosh\phi} \cdot V_{n+1} + \frac{Z \sinh n\theta}{\cosh\phi} \cdot I_{n+1},$$

$$I_1 = \frac{\sinh n\theta}{\cosh\phi} \cdot V_{n+1} + \frac{\cosh(n\theta-\phi)}{\cosh\phi} \cdot I_{n+1}.$$

But the matrix of this substitution is the nth power of the matrix of the preceding substitution. Hence the following theorem: given a matrix

$$\begin{vmatrix} a, & b \\ c, & d \end{vmatrix},$$

* *Cf.* M. Vaulot, *Revue Générale d'Electricité*, p. 493 (1927).
† J. I. E. E. 1927, p. 223.

of which the determinant is unity, its nth power is

$$\begin{vmatrix} \dfrac{\cosh(n\theta+\phi)}{\cosh\phi}, & \dfrac{Z\sinh n\theta}{\cosh\phi} \\ \dfrac{\sinh n\theta}{Z\cosh\phi}, & \dfrac{\cosh(n\theta-\phi)}{\cosh\phi} \end{vmatrix},$$

where Z, θ, and ϕ are chosen so that

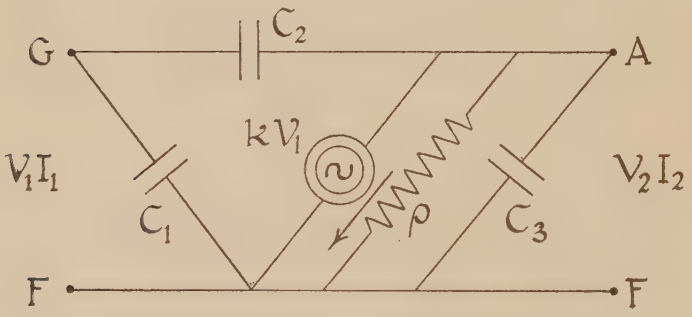
$$\cosh(\theta+\phi)/\cosh\phi = a,$$
$$Z\sinh\theta/\cosh\phi = b,$$
$$\sinh\theta/Z\cosh\phi = c,$$
$$\cosh(\theta-\phi)/\cosh\phi = d.$$

This result can be easily verified by induction.

2. *The Thermionic Valve.*

A thermionic valve has the equivalent circuit shown in fig. 2, where ρ is the internal resistance and k the mutual

Fig. 2.



conductance of the valve, while the sine wave within two circles is a constant current generator giving a constant current kV_1. If u is the impedance of C_1, v of C_2, and w the impedance of ρ and C_3 in parallel, then it is readily shown that

$$V_1 = \frac{w+v}{w(1-vk)}.V_2 + \frac{v}{1-vk}.I_2,$$

$$I_1 = \frac{w+u+v+uwk}{wu(1-vk)}.V_2 + \frac{u+v}{u(1-vk)}.I_2.$$

This, again, is a homogeneous linear substitution, but differs

from that of a passive network in that its determinant is not unity but is $1/(1-vk)$.

Let

$$1/(1-vk)=\sigma^2.$$

Then the matrix of this substitution may be written as

$$\sigma\begin{vmatrix} a, & b \\ c, & d \end{vmatrix},$$

where

$$a=\frac{\sigma}{w}(w+v),$$

$$b=\sigma v,$$

$$c=\frac{\sigma}{wu}(w+u+v+uwk),$$

$$d=\frac{\sigma}{u}(u+v),$$

and

$$ad-bc=1.$$

3. *The Multistage Valve Amplifier.*

Now consider a multistage valve amplifier made up of n stages. Let each stage consist of a valve whose matrix is

$$\sigma\begin{vmatrix} a, & b \\ c, & d \end{vmatrix},$$

followed by a passive coupling network whose matrix is

$$\begin{vmatrix} a', & b' \\ c', & d' \end{vmatrix}.$$

Then the matrix of a single stage will be

$$\sigma\begin{vmatrix} a, & b \\ c, & d \end{vmatrix}\times\begin{vmatrix} a', & b' \\ c', & d' \end{vmatrix}=\sigma\begin{vmatrix} \mathrm{A}, & \mathrm{B} \\ \mathrm{C}, & \mathrm{D} \end{vmatrix},$$

where

$$(\mathrm{AD}-\mathrm{BC})=1.$$

Hence, if we chose three constants, Z, θ, and ϕ, corresponding to A, B, C, and D, the matrix of a multistage amplifier of n such stages will be

$$\left\{\sigma\begin{vmatrix} \mathrm{A}, & \mathrm{B} \\ \mathrm{C}, & \mathrm{D} \end{vmatrix}\right\}^n=\sigma^n\begin{vmatrix} \dfrac{\cosh(n\theta+\phi)}{\cosh\phi}, & \dfrac{\mathrm{Z}\sinh n\theta}{\cosh\phi} \\ \dfrac{\sinh n\theta}{\mathrm{Z}\cosh\phi}, & \dfrac{\cosh(n\theta-\phi)}{\cosh\phi} \end{vmatrix},$$

and thus, if V_{n+1} and I_{n+1} are the output volts and current of the n stage amplifier,

$$V_1 = \frac{\sigma^n \cosh(n\theta+\phi)}{\cosh\phi} \cdot V_{n+1} + \frac{\sigma^n Z \sinh n\theta}{\cosh\phi} \cdot I_{n+1},$$

$$I_1 = \frac{\sigma^n \sinh n\theta}{Z\cosh\phi} \cdot V_{n+1} + \frac{\sigma^n \cosh(n\theta-\phi)}{\cosh\phi} \cdot I_{n+1}.$$

If the amplifier is terminated by an impedance z, then $V_{n+1}/I_{n+1} = z$, and if z_n is the sending-end impedance of the n stage amplifier terminated by z

$$z_n = \frac{V_1}{I_1} = Z \cdot \frac{z\cosh(n\theta+\phi) + Z\sinh n\theta}{z\sinh n\theta + Z\cosh(n\theta-\phi)}.$$

If y_n is the receiving-end impedance of the n stage amplifier terminated by z,

$$y_n = \frac{V_1}{I_{n+1}} = \sigma^n \cdot \frac{z\cosh(n\theta+\phi) + Z\sinh n\theta}{\cosh\phi}.$$

The voltage amplification will be

$$\frac{V_{n+1}}{V_1} = \frac{zI_{n+1}}{V_1} = \frac{z\cosh\phi}{\sigma^n\{z\cosh(n\theta+\phi) + Z\sinh n\theta\}}.$$

LXX. *Notices respecting New Books.*

Index Generalis: Annuaire général des Universités, Grandes Écoles, Bibliothequès, Instituts Scientifiques, Jardins Botaniques et Zoologiquès, Musées, Observatoires, Sociétés Savantes. Published under the direction of Dr. R. de Montessus de Ballore. [Pp. 2320.] (Paris: Editions Spes. 1929–30.) Price not stated.

The current volume of the 'Index Generalis' is the tenth of the series, which was commenced in 1919. It is now well-known as a comprehensive directory of the learned world. The present volume comprises: (1) Directories of universities, colleges, and professional schools, arranged according to countries, 1161 pages; (2) astronomical observatories, 86 pages; (3) libraries and archives, 276 pages; (4) scientific institutes and museums, 118 pages; (5) learned societies and academies, 190 pages; (6) list of exchanges, 7 pages; (7) index of names (60,000 persons), 423 pages; (8) geographical and other indices, 50 pages.

In addition to the names of professors, lecturers, teachers, scientific staff, and administrative officers, much miscellaneous

information is given, such as dates of foundation and number of students of universities, etc., instrumental equipment and programmes of observatories, lists of fellows and foreign members of the principal scientific societies, etc.

A proof of each entry is sent annually to the contributor in order to ensure that the Index is accurate and up-to-date.

A careful examination leads to the conclusion that the entries are reasonably complete. There are, however, a comparatively large number of errors in the extensive name-index—names spelt incorrectly, wrong initials, incorrect page stated, &c. The entries referring to Sir J. J. Thomson may be instanced : there are two separate entries "Thomson, J. J.," and two other entries "Thomson, Sir J. J.," all referring to the same person, though apparently to four separate persons ; a third entry "Thomson, J. J." is an error for "Thompson, J. J." Immediately preceding, under "Thomson, J. G.," are three entries, one of which refers to a J. H. Thomson. Many errors of such and similar natures were found, and it would appear that more careful editing and proof-reading of the index is required.

In spite of such defects, the volume provides an invaluable work of reference, the editing of which must have been a heavy task. The Index is published in two editions, the one French, the other English.

A Course of Analysis. By E. G. Phillips, M.A., M.Sc. [Pp. viii + 362, with 35 figures.] (Cambridge : at the University Press, 1930. Price 16*s.* net.)

A real need has been met by this book, which is intended for First Year Honour Students. There has not hitherto been any text-book in English which covers the same ground. The author, in his preface, remarks that "Since modern analysis requires great precision of statement and demands from the student a very clear understanding of its fundamental principles, I have aimed at presenting the subject in such a way as to make every important concept clearly understood." In this aim he has undoubtedly succeeded : the explanations of fundamental principles are very clear, and the essential steps in the logical arguments are carefully emphasized.

A brief account of the definition of number is given in Chapter I., including Russell's modification of Dedekind's method of defining an irrational number. Chapter II. is devoted to bounds and limits of sequences, and is followed by chapters on limits and continuity and on the differential calculus. Prominence is given to "differentials," a feature to be commended and one which has not been widely adopted in English text-books. The chapter on Inequalities is a

valuable one, and contains proofs of both Hölder's and Minkowski's inequalities, which have not been given previously in any English book. Two chapters deal with the integral calculus and its applications. Functions of more than one variable are next dealt with: here the conception of differentials leads to clarity and conciseness. The remaining chapters deal with implicit functions, double integrals, triple and surface integrals, and power series.

A student who works through this book intelligently and conscientiously cannot fail to have a thorough grounding in the subject, paving the way for the more advanced standard treatises. At the end of each chapter a series of examples have been given: these have been carefully selected to illustrate the fundamental concepts, and will prove of great value to teachers and lecturers.

An Introduction to Surface Chemistry. By E. K. Rideal. Second Edition. [Pp. xii + 460.] (Cambridge: at the University Press, 1930. Price 21*s.* net.)

The increasing importance of the study of the properties of interfacial phases, and the development of the subject as well on the theoretical as on the experimental side, have been responsible for a considerable increase—124 pages—in the new edition of this book, as compared with the first edition published nearly four years previously. The present edition gives full consideration to recent work, but, in addition, a thorough revision has been made and errors noted in the first edition have been corrected.

Dr. Rideal has given a masterly survey of the many and varied phenomena which depend ultimately upon the cohesive forces which hold solid and liquid masses together. To students of physical chemistry the book will prove invaluable; other scientific readers will find much of interest in the discussions of the phenomena dealt with and of their theoretical foundations. The arrangement of the material is logical and satisfactory. The surface energy and surface tension of liquids is dealt with in the first chapter, which is followed by others devoted to the surface tension of solutions and to phenomena dependent upon surface films. The properties of liquid-liquid interfaces are then discussed, including a full treatment of spreading and of emulsions. Chapters on gas-solid interfaces and liquid-solid interfaces follow. Electrical phenomena at interfaces are fully dealt with in the next chapter. The two remaining chapters are devoted to the theory and properties of colloids, including the theory of the Brownian movement and the structure of gels. Detailed name and subject indices are given; some errors in references to pages in these have been noticed.

Contributions to the History of Determinants, 1900–1920. By Sir Thomas Muir. (London: Blackie & Son, Ltd., 50 Old Bailey. Price 30*s.* net.)

The original plan to write a history of determinants to the end of the nineteenth century was completed by the publication of the fourth volume, seven years ago. The supplementary volume continues the history of the subject, and gives a record of the researches during the first two decades of the twentieth century on determinants in general, compound determinants, alternants, recurrents, and wronskians. The author's contributions to this volume include over a hundred papers on these special determinants.

Historical papers on other special forms*, which do not appear in this volume however, have been contributed by Sir Thomas Muir to the 'Proceedings' of the Royal Societies of Edinburgh and South Africa. Each paper is carefully reviewed, and points of historical interest recorded in the introductory remarks. The work of Kostka on symmetric functions and determinants, extending over a period of forty years, receives notice, in particular, his final memoir embodying his life's work on the subject. Unfortunately, no reference is made to the investigations of other workers in this field.

One chapter is devoted to notices of text-books, and a complete subject-index of the contributions reviewed in this volume and its predecessors is provided in an appendix.

It is a matter of congratulation that Sir Thomas Muir has had the opportunity of bringing his History of Determinants to recent times, and all students of mathematics, specialists or not, will recognize their indebtedness to him on this great achievement.

The Theory of Approximation. By Dunham Jackson, American Mathematical Society Colloquium Publications. Vol. XI. (New York: published by the American Mathematical Society, 501 West 116th Street.)

The Theory of Approximation has formed the subject of two important monographs by De la Vallée Poussin and S. Bernstein, with which Prof. Jackson's work has some points of contact. The approximate representation of continuous functions in terms of polynomials and trigonometric sums, and the convergence of Fourier and Legendre series are considered in the introductory chapter, followed by a discussion of the corresponding theorems for discontinuous functions, the degree of convergence of Fourier and Legendre series under the hypothesis of limited variation, and the convergence and degree of convergence of Fejér's arithmetic mean. Atten-

* Eleven in all—circulants, continuants, hessians, jacobians, etc.

tion is drawn to the relation between Fourier series and the principle of least squares, and to the remarkable theorems of Bernstein on the derivatives of trigonometric sums and polynomials. The polynomial theorem has been generalized in the case of developments in terms of characteristic functions of differential systems and in the polynomial approximation over an infinite interval. The next section deals with trigonometric interpolation, in which reference is made to the work of Faber and the extensions of Jensen to the case of Sturm–Liouville sums. In the final chapter the author gives an introductory exposition on the geometry of function space, and adds a list of all the important theorems which appear in the text.

The Quarterly Journal of Mathematics : Oxford Series. Vol. I. No. 1. April 1930. [Pp. 76.] (Oxford : at the Clarendon Press, 1930. Price 7*s.* 6*d.* net. Annual Subscription 27*s.* 6*d.* post free.)

The 'Quarterly Journal of Mathematics (Oxford Series)' is the successor to the 'Quarterly Journal of Mathematics' and 'The Messenger of Mathematics.' It is edited by T. W. Chaundy, W. L. Ferrar, and E. G. C. Poole, with the cooperation of A. L. Dixon, E. B. Elliott, G. H. Hardy, A. E. H. Love, E. A. Milne, F. B. Pidduck, E. C. Titchmarsh. These names should ensure the future success of the Journal, of which there will be no doubt if the standard of the first number is maintained. This contains important papers by E. A. Milne on "The Motion of a Fluid in a Field of Radiation," by O. Veblen on "A Generalization of the Quadratic Differential Form," by G. Pólya on "Some Problems connected with Fourier's Work on Transcendental Equations," and by Mary L. Cartwright on "The Zeros of Certain Integral Functions." The Journal in its new form is well printed on good paper, and we wish it a successful future.

The Material Culture and Social Institutions of the Simpler Peoples. An Essay in Correlation. By L. T. Hobhouse, G. C. Wheeler, and M. Ginsberg. [Pp. viii + 299.] (London : Chapman and Hall, Ltd., 1930. Price 10*s.* 6*d.* net.)

This work, which appeared originally in 1915, has long been out of print. The present republication, by the Replika Process, is necessarily identical with the original edition, so that it has not been possible to incorporate the results of the considerable amount of field-work in social anthropology which has been carried out in the intervening years. Nevertheless, the republication—summarizing as it does an enormous amount of data bearing on material culture and social institutions

of the more primitive races and tribes—will be welcomed by students of sociology and anthropology.

In the introduction the general problem of classifying such data is discussed and the various difficulties inherent in such a process are pointed out. The investigation itself is divided into four chapters. In the first the methods of classifying the simpler peoples according to their economic level are explained, and some 600 peoples or tribes are grouped into the following categories :—Lower Hunters, Higher Hunters, Incipient Agriculturals, Pure Agriculturals, Higher Agriculturals, and two forms of Pastorals. In the remaining chapters a tabulated morphology is provided of the institutions of these peoples, including government and justice, the family—embracing marriage, divorce, and the position and status of women—war, social structure, and property. The classifications given in each chapter are treated statistically, in order to discover the relations between economic growth and the development of the social order. The general correlation between social development and economic level are clearly brought out. The data are exhibited in a form which permits of ready verification, and extensive notes are given to each table of classification. The volume is of great value both as a summary of a mass of anthropological data and as a contribution to theories of social development.

Advanced Trigonometry. By C. V. Durell, M.A., and A. Robson, M.A. [Pp. viii + 336, with 79 figures.] (London : G. Bell and Sons, Ltd., 1930. Price 8*s.* 6*d.*)

The need of suitable school text-books in mathematics, in which the subjects are presented from the modern point of view, has been felt by many teachers. The volume under review is the first of a series by the same authors, which will include parallel volumes on advanced algebra, on calculus, and a companion volume on analysis, and which attempt to meet this need. The basic idea underlying the treatment is that advanced trigonometry should serve as an introduction to modern analysis ; thus the methods for expanding functions in series are used to draw attention to remainders and limits ; the idea of convergence is introduced at an early stage ; the reality of complex numbers is emphasized, etc. The proposed companion volume on analysis is intended to be used in conjunction with the present volume and to deal more fully with such matters as limits, continuity, convergence, etc.

The present volume has been carefully planned, and represents a serious attempt to provide a course which will not merely train the student in the manipulation of symbols, but which will give him also a real insight into the subject. Difficult points are not shirked, but are carefully explained.

There are many illustrative examples, some of which are worked out by three or four different methods. Each chapter contains a series of easy and a series of harder examples to be worked by the student. A key for the convenience of teachers is published (price 15*s.* net) in which solutions are given in considerable detail. The volume can be strongly recommended as an advanced text-book for schools.

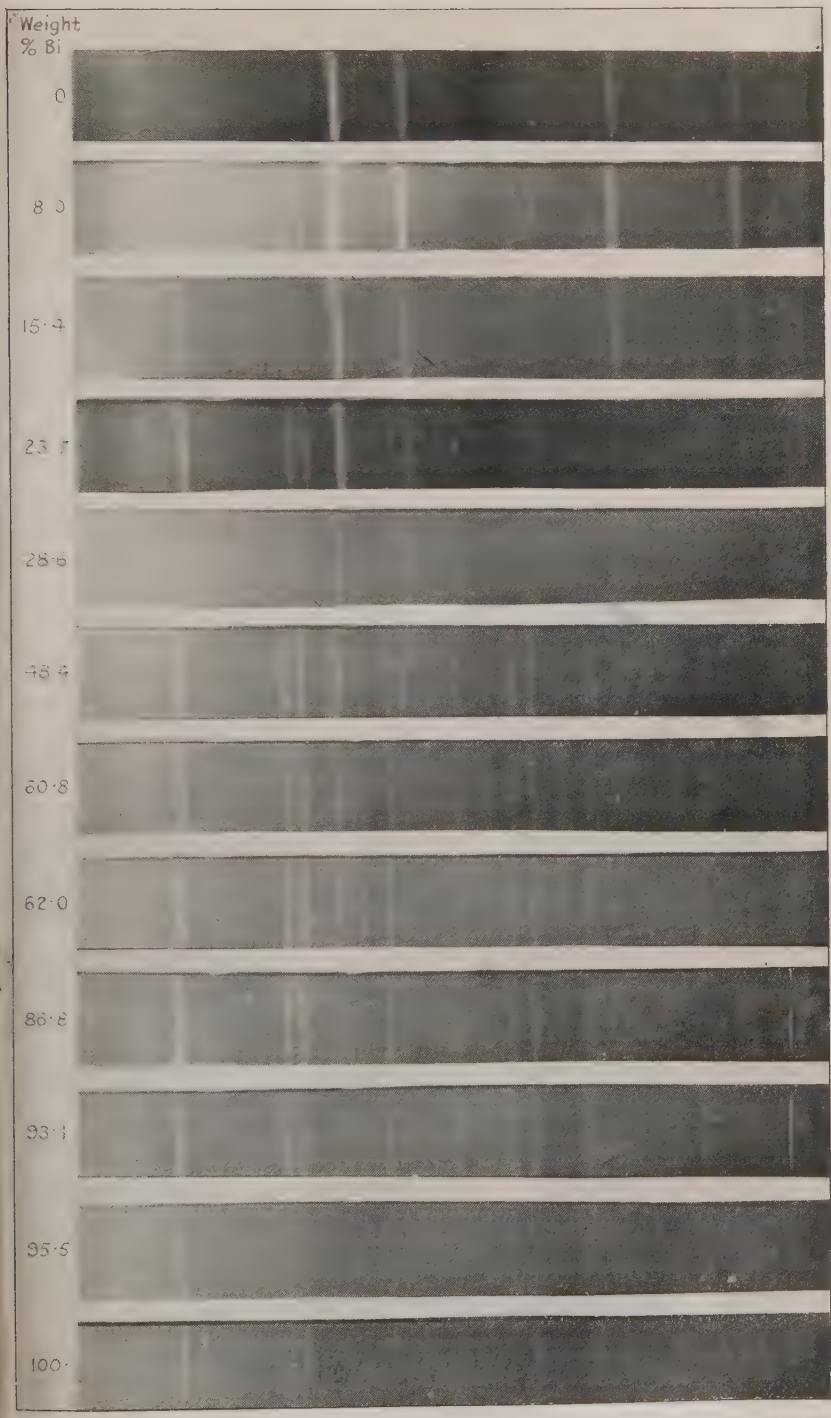
La Planète Mars, 1659–1929. Par E. M. Antoniadi. [Pp. 240, with 150 figures and 10 plates.] (Paris : Hermann et Cie, 1930. Price 80 fr.)

M. Antoniadi has been an assiduous observer of Mars for many years, and for more than twenty years has had the use of the large 83 cm. refractor at Meudon for such observations. His observations are summarized and discussed in the present monograph ; in addition he has summarized all the observations of the various topographical features obtained since the first sketches of Mars by Huyghens in 1659. These collected observations form the second and main portion of the monograph, which constitutes in effect a dictionary of Mars, which will be found indispensable by all observers of the planet.

The first portion is devoted to more general matter : old observations, methods of observation, numerical data, the surface spots, the canals, the polar caps, the atmosphere of Mars, its physical conditions and habitability, its satellites. M. Antoniadi is strongly convinced that the canals have no objective reality ; his own careful observations have failed to reveal them even under the best conditions, and he cites statements by many other acute observers who, with large instruments and under favourable conditions, have not been able to observe them. He considers, however, that they have a basis of reality, in irregular lines, more or less continuous and spotted, or in other irregular surface markings. M. Antoniadi rejects the temperatures found for Mars and other planets by bolometric methods as illusory ; although these run counter to the preconceived ideas of most planetary observers, it seems that they must be accepted. The agreement between modern observations made by different methods is surprisingly good, and Jeffreys has shown that they are in accordance with what would be anticipated theoretically.

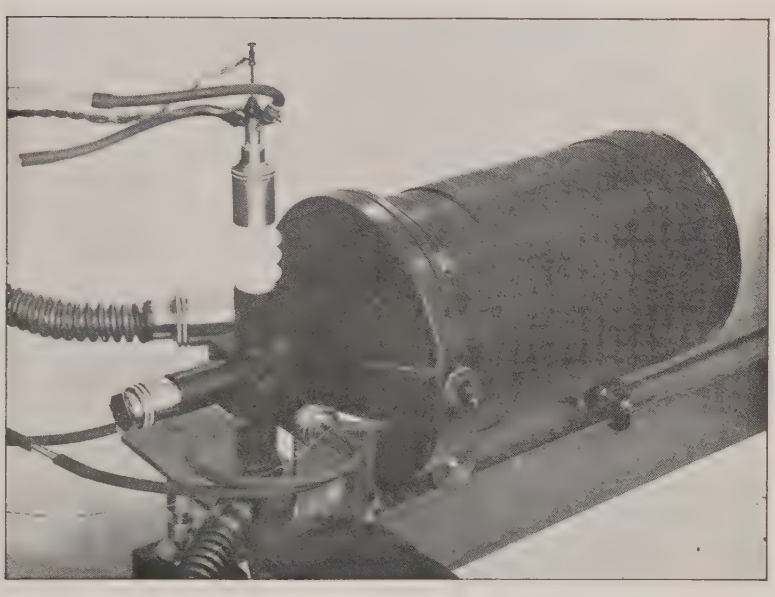
The volume is well illustrated with figures showing various details ; several composite drawings of the surface of the planet and of different regions are given in the form of plates. A large majority of the drawings are by the author himself. The volume forms an excellent summary of his own observations and of those of other observers of Mars.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]



Powder Photograms of the System Cu-Bi. Mo-K Radiation.

Fig. 2.

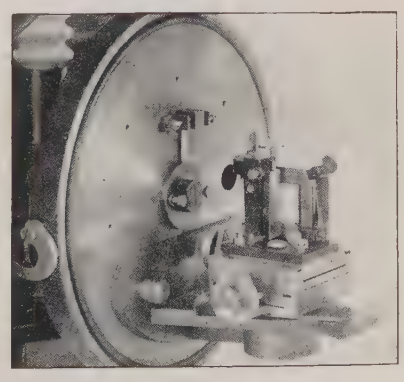


Vacuum Spectrometer for plane gratings.

Fig. 3.

Plate-holder and grating table.

Fig. 4.



The grating, mounted in its holder.

FIG. 7.

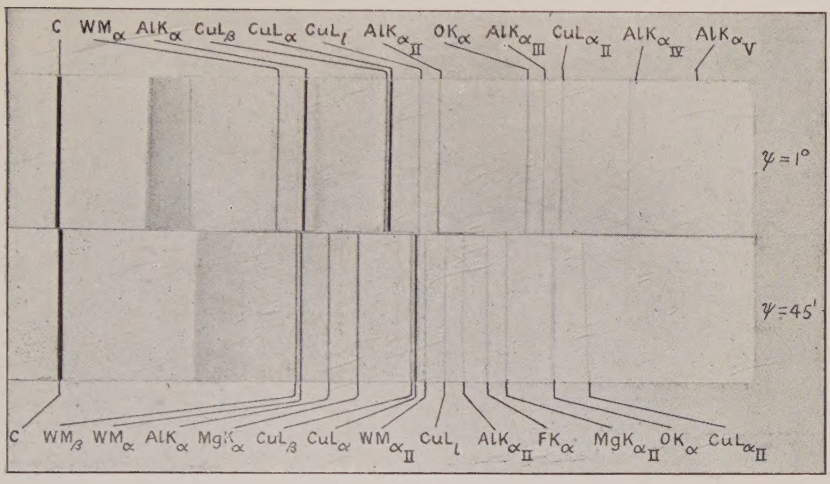
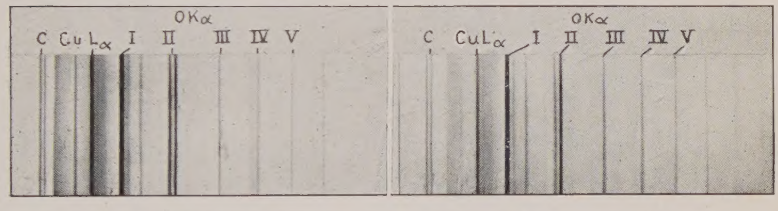
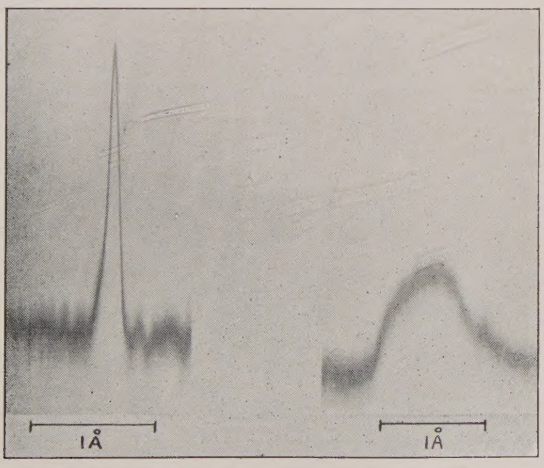

C WM$_\alpha$ AlK$_\alpha$ CuL$_\beta$ CuL$_\alpha$ CuL$_l$ AlK$_{\alpha_{II}}$ OK$_\alpha$ AlK$_{\alpha_{III}}$ CuL$_{\alpha_{II}}$ AlK$_{\alpha_{IV}}$ AlK$_{\alpha_V}$
$\psi = 1°$
$\psi = 45'$
C WM$_\beta$ WM$_\alpha$ AlK$_\alpha$ MgK$_\alpha$ CuL$_\beta$ CuL$_\alpha$ WM$_{\alpha_{II}}$ CuL$_l$ AlK$_{\alpha_{II}}$ FK$_\alpha$ MgK$_{\alpha_{II}}$ OK$_\alpha$ CuL$_{\alpha_{II}}$

FIG. 8.



Eclipse plate. Schumann plate.
Exposed under the same conditions.

FIG. 9.



Al K$_\alpha$. C K$_\alpha$.

Blackening curves from Al K$_{\alpha_{II}}$ and C K$_{\alpha_1}$. The small variations in the C K$_\alpha$-curve are apparently due to irregularities in the emulsion. They do not reappear when different parts of the line are micro-photometered.

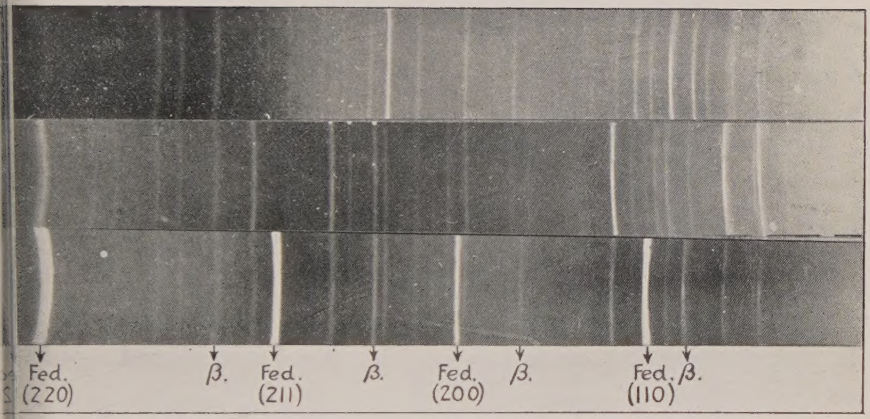


FIG. 1.

FIG. 2.

FIG. 3.